University of Alberta

Redistribution of Arsenic and Iron in an Acid Sulphate Soil, Alberta, Canada

by

Patricia Brost

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

Soil Science

Department of Renewable Resources

Edmonton, Alberta

Fall 2002

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ABSTRACT

Concentrations of arsenic and 20 other major and trace elements were evaluated at four positions along the catena of an acid sulphate soil in northwestern Alberta. The objective was to determine whether arsenic is being translocated down slope in soil porewater and accumulating in catchment basins that might be connected to water sources. Arsenic was generally elevated in concentration (average 34.6 $\mu g\ g^{-1}$) relative to most soils. It was unclear whether arsenic had been translocated down slope, as it was equally concentrated in B horizons at mid-slope and in an iron-rich layer (293,000 $\mu g\ Fe\ g^{-1}$) in the depression at the catena bottom. It was expected that arsenic would accumulate with the iron. Low arsenic concentrations in groundwater on site (average 0.4 $\mu g\ L^{-1}$), combined with lack of arsenic in the iron layer, suggest that competing ions, primarily sulphate, may have prevented much arsenic sorption. The main control of arsenic chemistry in this soil system appears to be pH and redox conditions.

ACKNOWLEDEMENTS

I would firstly like to thank Dr. Marvin Dudas, my supervisor, for his consistent, knowledgeable, and simple outlook on this project from beginning to end. Despite my confusion, ignorance, enthusiasm (at times), and/or frustration (at times), he guided me back to course. His support, expertise, and guidance were pivotal to the project. He provided a very valuable kind of teaching and presence that I am very grateful for. Thank you very much, Dr. Dudas. It has been a pleasure learning from you.

Dr. John Duke brought an essential and enjoyable component to the project with his analytical expertise, his geochemical knowledge, his Irish sense of humour, and his fervency for teaching. John spent hours tutoring me in various subjects, ranging from radiochemistry to petrology to geological (and other) trivia. I was honoured to be his pupil and only wish I could house the vast amount of knowledge he is willing to share. Thank you so much for your time, your patience, your attitude, and your friendship. And, please, continue to teach.

Thank you, Dr. Les Fuller, for serving on my supervisory committee. I was impressed by the quality of your input and advice. Your presence is calming and your words demand attention. It has been great working with you.

Thank you, Dr. Sylvie Quideau, for serving on my examining committee. Your demeanor is serene and unimposing, qualities that were welcome during the exam! Thank you for your time and contribution.

I extend a huge thank you to my work, Komex International Ltd., who has supported my grad school venture in various ways. I am extremely grateful and lucky to work for such a company and with such remarkable people.

I wouldn't have considered, pursued, or completed my masters if it wasn't for Laila Miller. Laila, your support, patience, encouragement, advice, and concern did not go unnoticed. I appreciate you and these things you provide with such ease.

Brent Mooder, Karen Mooder, Jacki McManus, Tannis Sharp, Morris Maccagno, Mark Trudell, Sean Murphy – thank you all for your concern, time, advice, patience, and encouragement. It was essential at times.

Thank you Michelle Cotton and Clara Qualizza. You were the ones who piqued my interest in soil science! What an honour for me to learn from two brilliant women who teach with such ease and have fun at the same time. You are both incredible role models.

Carrie Todd and Audrey Lanoue were (and are) angels on my shoulder. I cannot articulate the meaning of your friendship to me. Thank you a thousand times for listening, supporting, sharing, helping, laughing, and just for being you. You're the best.

I am extremely fortunate to have shared this grad school experience with Brooke Bennett, Tracy Muloin, and Marty Yarmuch. Without friends like you at school to lean on, hang out with, eat lunch with, complain with, etc., school would have been pretty dismal. You are all individually incredible people. Thank you for your friendship. I hope it continues far into the future.

I don't know that I want to so much thank my family as apologize. I am sorry you have been ignored for the better part of four years, especially the last one! Thank you for understanding, or, if not understanding, for tolerating. Mom, thank you for truly (amazingly!) being interested in my venture; Dad thank you for being you and for being such a good Dad, as always. Corinne and Trina, this has nothing to do with my thesis, just thanks for being such awesome sisters.

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1. INTRODUCTION

Elevated arsenic (As) in groundwater is a global health issue. The most severe problem is in India and Bangladesh, where millions of people suffer from As poisoning due to chronic ingestion of excessive As in drinking water. In the Cold Lake area of Alberta, elevated levels of As occur in groundwater, and considerable controversy exists as to the source of As and the mechanism of release to groundwater. Elevated As concentrations in soils or water may arise from anthropogenic sources, or they may be naturally-occurring, from As-rich bedrock.

The present research is a continuation of studies by Dudas *et al.*, who have described many characteristics of the anomalously As-rich Boundary Soils of northwestern Alberta. These researchers have examined many aspects of these soils, including: micromorphology and common chemical parameters (Pawluk and Dudas, 1978), the source of arsenic (Dudas, 1987), total and extractable As concentrations (Dudas *et al.*, 1988), the particle size fraction most strongly correlated with As (Dudas *et al.*, 1988), and the type of iron oxides (Dudas *et al.*, 1988) and phyllosilicates (Pawluk and Dudas, 1978; Dudas *et al.*, 1988) present.

While many characteristics of the Boundary Soils have been investigated and reported, the vertical and lateral distribution of As in the Boundary Soils has not previously been studied. Assessing the distribution of As in soils might reveal information about its mobility, which is of interest because of groundwater quality and health concerns. Thus, the objectives of this study were:

1. To determine whether down slope transport of As occurs, and, if so, whether this results in further enrichment of As in depressional areas that serve as surface water catchment basins. It was hypothesized that down slope transport of As may be occurring, resulting in increased concentrations in soil and /or groundwater in the depressional area.
2. To determine what mechanisms control the translocation of As.
3. To evaluate As geochemistry in the Boundary Soils by determining concentrations of other elements in the soils and assessing trends and interactions with As.

4. To compare element content of Boundary Soils and associated groundwater with other acid sulphate soils, Alberta soils, and groundwater.
5. To characterize the unique iron-rich layer present in the depression of the study site.

The information about As gained during this study will add to the understanding of As behaviour in soil and groundwater, and may be useful to predict As behaviour in other environmental situations.

2. LITERATURE REVIEW

2.1. SOURCES OF ARSENIC

Arsenic is a naturally-occurring element in the earth's crust and is more abundant than tin, mercury, and silver (Hurst, 1927). Although it is only the twentieth element in crustal abundance, it is ubiquitous (Cullen and Reimer, 1989), occurring in fresh water, groundwater, soils, sediments, the atmosphere, vegetation, fish, crustaceans, mammals, bread, and milk, for example (Rankama and Sahama, 1950).

It has been estimated that over 99 % of As in the environment occurs in rocks. Sedimentary rocks, especially those containing S (Boyle and Jonasson, 1973), have higher amounts of As than metamorphic or igneous rocks (Nriagu, 1994a). The arsenic content of sedimentary rocks ranges greatly, depending on the rock type. Sandstone and limestone are generally relatively low in As (1.5 to 2.3 $\mu g\ g^{-1}$); shale typically contains considerably more (2 to 42 $\mu g\ g^{-1}$; as reported in Onishi and Sandell, 1955), especially those containing Fe and/or S (up to 6,000 $\mu g\ g^{-1}$ has been reported; Boyle and Jonasson, 1973). Geothermal soils and waters (> 50 °C) are often associated with high levels of S and, as such, are also known to contain elevated concentrations of As; up to 1000 $\mu g\ L^{-1}$ has been reported in springs in Yellowstone National Park (Nriagu, 1994a; Welch *et al.*, 2000). In Alberta, As in many soils ranges from 4.0 to 6.5 $\mu g\ g^{-1}$ (Dudas and Pawluk, 1980).

The most common As-containing minerals are arsenopyrite (FeAsS), realgar (AsS), orpiment (As_2S_3), niccolite (NiAs), and cobaltite (CoAsS; Sisler *et al.*, 1959; Boyle and Jonasson, 1973). However, pyrite (FeS_2) is the main host of As in rocks; As must comprise a sizeable portion (about half) of pyrite in order for the mineral to be considered arsenopyrite (Read, 1974). Next to sulphide minerals, As is commonly associated with oxides of Fe, Mn, and Al (due to their great adsorptive capacity), and with organic carbon (due to its ability to chelate with As; Boyle and Jonasson, 1973; Kabata-Pendias, 2001).

Human activity has disrupted the distribution of As in the environment. The amount of As entering the oceans has increased by a factor of three, mainly through the use of As-containing pesticides, by mining As-rich ores, by burning fossil fuels (Ferguson and Gavis, 1972; Pierce and Moore, 1982), and through the use of As in glass

production (Welch *et al.*, 2000) and as a wood preservative (Cullen and Reimer, 1989). Arsenic-containing pesticides, such as MSMA (monosodium methanearsonate), DSMA (disodium methanearsonate) and cacodylic acid (dimethyl arsinic acid), were widely used in the agriculture industry from the 1920s until the 1980s. However, by 2000, because of environmental concerns, the use of As-containing chemicals in agriculture had been reduced to 10 % of its peak use. Lead arsenate was commonly used as an orchard insecticide until the introduction of DDT in 1947 (Welch *et al.*, 2000). In the mining industry As is commonly found with Pb, Zn, Au, and Cu ores and can be released during the smelting process (Pierce and Moore, 1982; Nriagu, 1994a). It is also frequently associated with bitumen, coal, and oil and can be introduced to the environment *via* fossil fuel utilization (Pierce and Moore, 1982; Cullen and Reimer, 1989). Arsenic, in the form of chromated copper arsenate (CCA), is still widely used as a preservative to prevent biological decay of wood (Cullen and Reimer, 1989) in Canada [Canadian Council of Ministers of the Environment (CCME), 1999] and the United States (Welch *et al.*, 2000).

2.2. Properties and Behaviour of Arsenic

Arsenic has a melting point of 817 °C, a boiling point of 614 °C, a density of 5.22 g cm^{-3}, and an electronegativity of 2.18 (Chemical Rubber Company, 1997). It is a member of Group VA of the periodic system, along with N, P, Sb, and Bi. Due to chemical similarities to these elements, As often exhibits chemical behaviour like P and Sb (Boyle and Jonasson, 1973). In the periodic table, As is located between the metals and the acid-forming elements and, as such, expresses both metallic and non-metallic properties (CCME, 1999). It is found in a variety of compounds, from oxides and sulphides to Cu-, Co-, Pt-, and Ag-containing minerals (Hurst, 1927).

Arsenic can occur in four oxidation states: arsine (-3), arsenic metal (0), arsenite (3+), and arsenate (5+; Boyle and Jonasson, 1973; CCME, 1999; Kabata-Pendias, 2001). In soil As is usually present in either the 3+ [As(III)] or 5+ [As(V)] oxidation state, the former being more toxic, soluble, and hence mobile than the latter (Ferguson and Gavis, 1972; Cullen and Reimer, 1989; Masscheleyn *et al.*, 1991). Arsenic (III) manifests its toxicity by forming strong, stable bonds to S-groups in proteins and enzymes (Ferguson and Gavis, 1972; Planer-Friedrich, 2001), thus preventing normal functioning and resulting in the disruption of the body's biochemistry. Although As usually occurs in an

inorganic form, organic compounds of As have been identified in the atmosphere, fresh water, sediments, soils, and biological tissue (Cullen and Reimer, 1989). Unlike many organotoxins, As does not bioconcentrate along the food chain, yet individual organisms can accumulate As (Ferguson and Gavis, 1972).

Arsenic can be oxidized, reduced, methylated, and demethylated (Nriagu, 1994a); the latter two processes being solely biologically driven (Ferguson and Gavis, 1972; as reported in Sadiq, 1997). Bacteria often expedite a process (*e.g.*, oxidation of arsenite to arsenate) that can occur in their absence (Kabata-Pendias, 2001). Under anaerobic conditions, arsenic can be microbially reduced to various gaseous, volatile, methylated arsenic compounds [*e.g.*, $(CH_3)_2AsH$, $(CH_3)_3As$] that can be released to the atmosphere (Ferguson and Gavis, 1972; reported in Sadiq, 1997; Kabata-Pendias, 2001). Microorganisms can exert a strong influence on As transformations in soil, thus affecting its accumulation, mobility, and toxicity.

It is well established that the most important controls on As behaviour in the environment are pH, redox potential (Eh), and aluminum and iron oxides chemistry (Pierce and Moore, 1982; Masscheleyn *et al.*, 1991; Nriagu, 1994a; Nickson *et al.*, 1998). Arsenic tends to be present in soil solution as arsenous acid species; the lower the pH, the more protonated the species. In soil solution of pH 3 to 6, $H_2AsO_4^-$ is the dominant form of arsenic; as pH increases to 7 and 8, both $H_2AsO_4^-$ and $HAsO_4^{2-}$ are abundant. Between pH 8 and 11, mostly $HAsO_4^{2-}$ is present (Sadiq, 1997). Generally, soil systems with high pH tend to adsorb less As, resulting in more As in soil solution; soils with low pH tend to sorb more As (Masscheleyn *et al.*, 1991; Welch *et al.*, 2000). This is because, at lower pH, the surfaces of clay minerals and iron oxides become protonated, with a net positive charge, thus developing an affinity for the As oxyanions (Sposito, 1989; Sadiq, 1997). Of course, pH interacts with other parameters to influence As behaviour.

Eh, combined with pH, govern which As species are present in the environment, which, in turn, determines the solubility, mobility, and toxicity of As. The As species that were described above as commonly being present in soil solution were As(V) species, occurring under oxic conditions. As Eh decreases (to around 250 mV), arsenate can be reduced to arsenite, and arsenious acid species (*e.g.*, $H_2AsO_3^-$, $HAsO_3^{2-}$; the degree of protonation depends on pH) become more stable (Ferguson and Gavis, 1972).

Because As(III) species tend to be more soluble than As(V) species, there will generally be more As in solution as Eh decreases (Masscheleyn *et al.*, 1991; Stein *et al.*, 2000). At Eh values around 0 mV, As sulphide compounds (*e.g.*, AsS^{2-}, As_2S_3, $HAsS_2$), which have low solubilities, may be present (Ferguson and Gavis, 1972). At very low Eh and pH values (less than –250 mV and 4, respectively; conditions rare in natural soil systems), arsine gas (AsH_3; Sadiq *et al.*, 1983) and methylated arsenicals may form (Sadiq, 1997).

The most common iron oxides found in soils are hematite (Fe_2O_3) and goethite (FeOOH), which occur as amorphous coatings on soil particles. These minerals are responsible for the red and brown colours characteristic of many soils (Bohn *et al.*, 2001). Aluminum and Fe oxides and oxyhydroxides strongly adsorb As (Jacobs *et al.*, 1970; Livesey and Huang, 1981; Pierce and Moore, 1982; Dudas *et al.*, 1988; Cullen and Reimer, 1989; Masscheleyn *et al.*, 1991; McGeehan, 1996; Kabata-Pendias, 2001). Adsorption increases under low pH conditions, when these minerals have a net positive surface charge (Sadiq, 1997). Arsenic has an exceptionally strong affinity for iron oxides, likely because iron oxides develop a greater positive surface charge under a wider range of pH (8.6 and lower) than do aluminum oxides (6 and lower) and manganese oxides (4 and lower; Sadiq, 1997). No maximum As adsorption by amorphous $Fe(OH)_3$ was observed by Pierce and Moore (1982), even for the highest concentrations of As studied. Dudas (1987) found Fe-enriched soil samples contained up to 450 μg As g^{-1}. Jacobs *et al.* (1970) found As sorption increased as free iron oxide content increased. Livesey and Huang (1981) concluded that the adsorption of As by four Saskatchewan soils was directly related to their Al content.

Arsenic behaviour in soil is also influenced by the presence of P, either naturally-occurring or originating from fertilizers and wastes (Livesey and Huang, 1981; Welch *et al.*, 2000). Arsenic and P are both polyvalent Group V elements and, as such, tend to exhibit similar physical and chemical properties (Boyle and Jonasson, 1973; Woolsen *et al.*, 1973). Phosphorous competes with As for adsorption sites, resulting in more As in solution in the presence of P than in its absence (Livesey and Huang, 1981; Welch *et al.*, 2000). Phosphorus displaces As more readily than As displaces P, as P has a greater affinity for alumina (Sieling, 1946) and forms more stable complexes with it than does As (Swenson *et al.*, 1949). Unlike P, As does not tend to form organic complexes in soil.

The ability of As to be methylated and volatile is also dissimilar to that of P (Sadiq, 1997).

2.3. History and Uses of Arsenic

Arsenic has been known for about 3000 years (Boyle and Jonasson, 1973). It was originally thought to be a type of S (Boyle and Jonasson, 1973), as As metal was first obtained by roasting one of its sulphide ores (Smith *et al.*, 1992). The word "arsenic" was derived from the Latin word "arsenikon" meaning "potent" (Boyle and Jonasson, 1973). Arsenic is perhaps best known for use as a poison, being colourless, odorless, and tasteless in the trioxide form. Historically, As was used for many purposes, such as in bronzing, in pigments and dyes, and, most commonly, as a remedy for many ailments, including anorexia, rheumatism, asthma, tuberculosis, diabetes, fever, skin disorders, hematologic abnormalities, sleeping sickness, syphilis (Planer-Friedrich, 2001), and as a general stimulant (Bates *et al.*, 1992). Throughout its history, As has also been used in explosives (Hurst, 1927), herbicides, insecticides, glass, wood treatment chemicals, and chemical warfare (Ferguson and Gavis, 1972; Cullen and Reimer, 1989; McGeehan, 1996; Welch *et al.*, 2000).

In Canada, white As (arsenious oxide), a by-product of smelting operations, was stockpiled in the early 1900s. In 1919, it was discovered that calcium arsenate was the most economical and efficient insecticide to keep the boll weevil, an insect that was destroying the southern United States cotton crops, in check. As a result, the stockpiled As was used to manufacture As-containing insecticides for various international crops: vines in France, rubber plants in the East Indies and the Malay Peninsula, coffee plants in Brazil, and grasses in South Africa, Argentina, and Australia (Hurst, 1927). The use of As dramatically declined in the early 1980s due to environmental concerns, and, in Canada today, As is mainly used in metallurgy and as a wood preservative (CCME, 1999).

2.4. Toxicity of Arsenic

The toxic effects of As on humans are well known. A dose of 300 mg of inorganic As can be lethal to an adult (Riewe *et al.*, 2000). In 1556, it was observed that arsenical cobalt corroded the skin of workers (Smith *et al.*, 1992). One of the first known carcinogens was inorganic As. In 1879, it was reported that German mine workers had a

high incidence of lung cancer that may have arisen from inhaling As during mining operations (Bates *et al.*, 1992). It was reported in 1888 that patients developed carcinoma of the skin after receiving treatments containing As for various skin conditions (Smith *et al.*, 1992). Other skin diseases, such as gangrene, keratosis, and hyperpigmentation (extreme cases of which are called "blackfoot disease") are symptoms of chronic As ingestion (Bates *et al.*, 1992) as are anemia, diabetes, nerve and blood vessel damage, and digestive disorders (Riewe *et al.*, 2000). Today, researchers are increasingly finding evidence to suggest that cancers of the liver, bladder, and kidney may also arise following persistent exposure to inorganic As (Smith *et al.*, 1992; CCME, 1999).

Estimates of total intake of inorganic As range from 0.18 to 0.73 $\mu g\ kg^{-1}$ body weight per day for adults (CCME, 1999). Both organic and inorganic As are present in varying amounts in food, usually in the nanogram per gram range. However, marine fish tend to contain relatively high concentrations of As (up to 3000 $ng\ g^{-1}$ has been reported; CCME, 1999). Usually the form of As in organisms is organic, which is less toxic than inorganic forms (Smith *et al.*, 1992; CCME, 1999). Soil As content generally ranges from 0.2 to 40 $\mu g\ g^{-1}$; urban air concentrations of As are usually around 0.02 $\mu g\ m^{-3}$ (Smith *et al.*, 1992).

The main exposure pathway for humans is ingestion of As in drinking water (Smith *et al.*, 1992). Although most major drinking water supplies in the United States contain As levels lower than 5 $\mu g\ L^{-1}$, it has been estimated that about 350,000 people in the US may be drinking water containing more than 50 $\mu g\ As\ L^{-1}$ (Bates *et al.*, 1992; Smith *et al.*, 1992), the former US and current World Health Organization (WHO) standard. This type of exposure translates to a one in 1000 chance of developing cancer as a consequence (Riewe *et al.*, 2000). In February 2002, the 50 $\mu g\ L^{-1}$ US drinking water standard, established in 1942, was lowered in to 10 $\mu g\ L^{-1}$ (Richardson, 2002).

Ingested As(V) is reduced to As(III), which is detoxified in the liver *via* methylation, and then excreted in the urine. Elemental and organic forms of As are efficiently eliminated from the body; whereas absorbed inorganic As tends to be stored in the lungs, liver, kidney, spleen, and skin (CCME, 1999). Due to its consistent carcinogenicity, inorganic As compounds have been classified in Canada as Group 1 carcinogens, that is "carcinogenic to humans", and as non-threshold toxicants, *i.e.*, any

dosage of which are believed to cause adverse health effects (CCME, 1999). Arsenic is considered one of the main environmental causes of cancer mortality in the world (Smith *et al.*, 1992).

Arsenic is known to be phytotoxic. However, the concentration of As that causes toxic effects in plants varies widely and depends on the plant type (Woolsen *et al.*, 1973; Cullen and Reimer, 1989; Kabata-Pendias, 2001), soil type (CCME, 1999), species of As present (Woolsen *et al.*, 1971), and distribution of As within the plant (*e.g.*, roots versus leaves; Cullen and Reimer, 1989). Douglas fir has been reported to commonly store more than 1000 μg As g^{-1}; whereas Woolsen *et al.* (1971) observed growth reduction in spinach plants exposed to 10 μg As g^{-1}. Conversely, some plants may even be stimulated by As (Woolsen *et al.*, 1971).

2.5. Arsenic in Groundwater

2.5.1. Scope of Problem

High concentrations of As in drinking water have caused deleterious health problems to millions of people around the world. The most serious examples are in India and Bangladesh, where millions of people have been drinking water contaminated with As since about 1993 (World Bank, 1999). As a result, millions of people have experienced adverse health effects, including skin lesions, keratosis, gangrene, and various forms of cancer. In these areas, the unusually high levels of As are naturally occurring, as the aquifers from which the water is drawn from are sulphide-rich, which have high As concentrations (Acharyya *et al.*, 1999). China, Ghana, Hungary, Taiwan, Thailand, Argentina, Chile, Mexico, the United States, and Canada also have areas with high As in the groundwater (Nriagu, 1994b; WHO, 1999). In Chile, cases of As-caused skin lesions were reported in the 1970s; by 1998 the link between high arsenic consumption and an increase in the incidence of bladder and lung cancer was confirmed. In Taiwan, recent studies have suggested that internal cancers, including bladder, kidney, liver, and lung, may be a result of ingestion of drinking water containing As (reported in Smith *et al.*, 1998). Classic symptoms of As poisoning (skin lesions, skin cancer, circulatory disorders) have been reported in Mexico, the United States, and Canada (Nriagu, 1994b).

While the majority of groundwater in the United States has low concentrations of As (< 1 μg L^{-1}), about 10 % of 30,000 groundwater samples analyzed for As from all over the United States had concentrations above 10 μg As L^{-1} (Welch *et al.*, 2000). In Alberta, 2.5 % of 824 groundwater samples tested in 1995-1996 exceeded the water quality guideline (Interim Maximum Acceptable Concentration; CCME, 1999) of 25 μg As L^{-1} (Fitzgerald *et al.*, 1997).

2.5.2. Sources of Arsenic to Groundwater

Elevated levels of As in groundwater may arise from natural or anthropogenic sources. The primary natural sources of As are sulphide minerals, particularly pyrite. In some areas of the United States, such as Oregon, Nevada, Utah, and California, high levels of As in shallow groundwater are thought to be due to the dryness and evaporative concentration of dissolved solids (Welch *et al.*, 2000).

Anthropogenic activities, such as mining, may cause naturally present As to become soluble and enter the groundwater. It is not generally known whether the use of manufactured As products, such as pesticides and wood preservatives, has resulted in significant As contamination of groundwater (Welch *et al.*, 2000). There are known cases where As in water is caused by the disposal of certain wastes, such as cotton gin and poultry and swine wastes (Welch *et al.*, 2000).

2.5.3. Mechanism of Arsenic Release to Groundwater

Welch *et al.* (2000) report that the most common cause of regionally elevated As concentrations in groundwater in the United States is arsenic release from iron oxides, by either desorption or dissolution. Oxidation of As-rich sulphide minerals, like pyrite, can release As and iron oxides. In an oxidized environment, the released As will be sorbed by the iron oxides. If conditions remain oxidized, the strongly sorbed As will be prevented from entering the aqueous phase. However, should anoxic conditions occur, as they commonly do in deep groundwater, the iron oxides will be reduced and release Fe and As into solution (Nickson *et al.*, 2000; Welch *et al.*, 2000). Additionally, iron oxides can be dissolved by petroleum products and landfill wastes, releasing As into solution (Welch *et al.*, 2000).

Many species of microorganisms can reduce iron oxides. Microorganisms utilize organic carbon for energy and generate electrons during the metabolic process. Under

aerobic conditions, these electrons are transferred to O_2. Once O_2 has been depleted, the electrons are transferred to NO_3^-, then MnOx, and then Fe(III)Ox. Ferric iron [Fe(III)] is reduced to ferrous iron [Fe(II)], which goes into solution. From there, it may precipitate as a solid, or be re-oxidized if it encounters oxic conditions (Schwertmann and Taylor, 1989).

After much debate, scientists studying the problem in India and Bangladesh have concluded that this is the mechanism of As release to groundwater in the aquifers supplying drinking water in those countries (Nickson *et al.*, 2000; McArthur *et al.*, 2001). Peat deposits present in the aquifer sediments are metabolized by microorganisms, resulting in depletion of O_2 and NO_3^-, and subsequent use of iron oxides for an electron receptor. Dissolution of the As-rich iron oxides releases As and ferrous iron to solution. Both the metabolism of organic carbon and iron oxyhydroxide reduction are shown in the following reaction:

$$4FeOOH + CH_2O + 7H_2CO_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 6H_2O$$

(Nickson *et al.*, 2000).

The original sources of As in India and Bangladesh are thought to be coal seams in the Rajmahal basin (which contain up to 200 μg As g^{-1}; Acharyya *et al.*, 1999) or sulphides in the Darjeeling Himalayas (which contain up to 8,000 μg As g^{-1}; Acharyya *et al.*, 1999). Both are connected to the Ganges river system, which supplies public water to Bangladesh and West Bengal (Acharyya *et al.*, 1999).

Cases of high concentrations of As in groundwater and soil have also been reported in Canada. West of Cold Lake, Alberta, levels of As up to 64 μg L^{-1} occur in groundwater wells less than 35 m deep. The source of the arsenic is the pyritic marine shale bedrock underlying the area. Low redox conditions in the aquifers, occurring within the bedrock, cause dissolution of iron oxides and release of the adsorbed As (Stein *et al.*, 2000). Soils with naturally elevated levels of As include those in the Peace River area of Alberta. These soils of the Boundary Series are the focus of this thesis.

2.6. BOUNDARY SERIES SOILS

2.6.1. Introduction

Soils of the Boundary Series of the Peace River region of Alberta (hereafter referred to as 'Boundary Soils') are unusual in that they contain naturally elevated levels of As. The Boundary Soils typically contain between 30 to 50 μg As g^{-1} soil (Dudas, 1984), whereas concentrations for other Alberta soils usually range from 4.0 to 6.5 μg As g^{-1} (Dudas and Pawluk, 1980). The As in these soils could cause deleterious health effects if it became soluble, entered the groundwater, and was subsequently used for livestock watering and/or human consumption. However, relatively little is known about the movement of As in these soils and, hence, the level of potential hazard. The main focus of this thesis was to examine the distribution and mobility of As in the Boundary Soils.

2.6.2. Regional Setting

The Boundary Soils have formed on outcrops of soft, grey, pyritic, silty marine shale of the Kaskapau Formation of Cretaceous age. The shale contains ironstone partings, and is interbedded in the lower part with fine-grained quartzose sandstone and thin beds of ferruginous oolitic mudstone (Green *et al.*, 1970). Due to its shale content, groundwater availability in the Kaskapau Formation is very low, with an expected yield of < 0.1 L s^{-1}. The hydrochemistry of the groundwater is $CaSO_4$ or Na_2SO_4, with SO_4^{2-} constituting greater than 60 % of the anions. The water tends to have high total dissolved solids (2,000 to 4,000 mg L^{-1} and greater) and is generally of poor quality (Ozoray, 1982).

Soils surrounding the Boundary Soils are mainly Dark Grey Solods, Gray Solods (formerly Grey Wooded Solod), and Humic Luvic Gleysols (formerly Humic Eluviated Gleysol; Reeder and Odynsky, 1965). The Boundary Soils are grey and dark grey acidic, shaly, silty clay loam to silty clay (Reeder and Odynsky, 1965). They are moderately well drained on undulating and strongly rolling topography (Scheeler and Odynsky, 1968). Boundary Soils are given a rating of 4 for soil capability for agriculture, which corresponds to poor to fair arable pasture and woodland (Reeder and Odynsky, 1965); they have low fertility due to low base saturation and exchange capacity (Farstad *et al.*, 1965). These soils are generally undesirable due to fine textures, poor physical condition,

imperfect drainage, frequent frost formation, and high clearing costs (Farstad *et al.*, 1965).

2.6.3. Boundary Soil Characteristics

The Boundary Soils occur on knoll top and side slope positions (Dudas, 1987). Vegetation consists of aspen trees, which are stunted due to nutrient depletion, and little understory growth (Bulmer, 1987). The Boundary Soils have low base saturation, with basic cations, such as Ca^{2+}, K^{+}, Na^{+}, and Mg^{2+}, occupying less than 10 % of the exchange complex (Pawluk and Dudas, 1978). The soils tend to accumulate secondary iron oxides in the B horizon and crystals of selenite in the C horizon (Dudas *et al.*, 1988). Boundary Soils have also been characterized as being composed primarily of clay to heavy clay with some eluviation of phyllosilicates, in particular smectite, muscovite, kaolinite (Dudas *et al.*, 1988), mica, and vermiculite (Pawluk and Dudas, 1978).

2.6.4. Classification of the Boundary Soils

The soils of the Boundary Series do not properly fit into any soil order of The Canadian System of Soil Classification (Agriculture Canada, 1987). According to Alberta Soil Series Working Group (1993), the Boundary Soils are classified as Orthic Grey Luvisols; as a result of their investigations, Pawluk and Dudas (1978) called the soils Dark Grey Luvisols. Historical soil surveys described the Boundary Soils as "undifferentiated podzolic" (Reeder and Odynsky, 1965; Farstad *et al.*, 1965) or "podzolic complex" (Scheeler and Odynsky, 1968). They do not fit into the Podzolic Order due to the iron originating from pyrite oxidation, rather than from podzolization, a process where Fe and Al are removed from the upper profile and settle in the B horizon more rapidly than does SiO_2 (Reeder and Odynsky, 1965). These soils meet the main requirement of a Luvisol, having a proper Bt horizon from clay eluviation; however, their low base saturation and high amount of extractable Fe exclude them from the Luvisolic Order (Pawluk and Dudas, 1978). Thus, there remains uncertainty as to the taxonomy and genesis of these soils.

2.6.5. Acid Sulphate Soils

Soils generated from oxidation of sulphide minerals are known as acid sulphate soils. They are sometimes called "cat clays", a term derived from the Dutch name for these soils ("Katteklei"; Bloomfield and Coulter, 1973). Usually, pyrite (FeS_2) is the

main sulphide mineral in potential acid sulphate soils, with concentrations of approximately 1 to 5 % by mass (van Breemen and Buurman, 1998). These soils occur around the world, occupying approximately 12 million hectares (ha) of land. Acid sulphate soils cover an estimated 600,000 ha of the Bangkok Plain in Thailand (Dent, 1986) and 1.8 million ha of the Mekong delta in southern Vietnam (Gustafsson and Tin, 1994).

Pyrite formation requires the following conditions:

- a population of sulphate-reducing bacteria;
- an anaerobic environment (sulphate reduction can only occur in the absence of oxygen);
- a source of dissolved sulphate (pyrite will only form if sufficient sulphate is available; usually, sea water or brackish water supply an adequate amount of sulphate);
- metabolizable organic matter [sulphate-reducing bacteria (*Desulfovibrio spp.*) require a source of carbon to utilize as energy for sulphate reduction];
- presence of iron minerals (Pons *et al.*, 1982; Dent, 1986; van Breemen and Buurman, 1998).

Usually, the types of environments that provide these conditions are recent coastal plains and inter-tidal swamps (van Breemen and Buurman, 1998). If Fe_2O_3 is the iron mineral and CH_2O is organic matter, pyrite may form as follows:

$$Fe_2O_3 + 4SO_4^{2-} + 8CH_2O + \tfrac{1}{2} O_2 \rightarrow 2FeS_2 + 8HCO_3^- + 4H_2O$$

(Dent, 1986; van Breemen and Buurman, 1998).

Sulphate reduction, oxidation of sulphide (S^{2-}) to disulphide (S_2^{2-}), and reaction of S^{2-} and S_2^{2-} with Fe minerals are essential steps in pyrite formation (Pons *et al.*, 1982).

Pyrite is only stable under anaerobic conditions; therefore, conditions allowing for the presence of O_2 will initiate pyrite oxidation (Dent, 1986). Examples of such conditions include drainage of the pyritic area, or deliberate exposure of sulphide minerals, such as that which occurs when mining sulphide ores.

Pyrite oxidation occurs in several stages, involving both chemical and microbiological components (Dent, 1986). The initiating phase produces ferrous iron and elemental S:

$$FeS_{2(aq)} \rightarrow Fe^{2+}_{(aq)} + S_2^{o} + 2e^{-}$$

The acid-generating phase produces sulphuric acid from the oxidation of elemental S:

$$S_2 + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^{+}$$

Ferrous iron is oxidized to ferric iron in the presence of oxygen by *Thiobacillus ferrooxidans*:

$$Fe^{2+} + \tfrac{1}{4}\, O_2 + H^{+} \xrightarrow{\textit{Thiobacillus ferrooxidans}} Fe^{3+} + \tfrac{1}{2}\, H_2O$$

The catalytic phase involves ferric iron acting as an oxidizing agent and continuing the oxidation of pyrite, which generates more acidity:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^{+}$$

(Nordstrom, 1982).

Oxidation of pyrite by ferric iron is limited by pH, as it is only soluble at pH less than 4, and *Thiobacillus ferrooxidans* will not survive at higher pH.

Thus, pyrite oxidation is an acidifying process, reducing the pH level to less than 3.5 during the active stages. The more O_2 available, the more sulphuric acid produced. The low pH causes dissolution of silicates and other minerals, and subsequent formation of secondary minerals, such as gypsum and jarosite (Carson *et al.*, 1982). Gypsum may form in acid sulphate soils during attempted acid neutralization by $CaCO_3$:

$$CaCO_3 + 2H^{+} + SO_4^{2-} + H_2O \rightarrow CaSO_4 \bullet 2H_2O + CO_2$$

(Dent, 1986).

Iron sulphate generated from pyrite oxidation may combine with K to form jarosite [$KFe_3(SO_4)_2(OH)_6$]. Jarosite forms under conditions where Fe(III) is stable (Eh greater than 400 mV; pH less than 3.7; Dent, 1986), and is, therefore, usually observed in fractures and on ped faces, where O_2 has access (Carson *et al.*, 1982; Dent, 1986). Formation of jarosite is regarded as an indication that a soil has undergone acid sulphate weathering but no longer has extremely low pH (Wagner *et al.*, 1982).

Jarosite tends to accumulate above the pyritic horizon and is recognizable as a conspicuous yellow precipitate (van Breemen and Buurman, 1998). Its formation may occur as follows:

$$6Fe_2(SO_4)_3 + O_2 + 22H_2O + 4K^+ \rightarrow 4KFe_3(SO_4)_2(OH)_6 + 10H_2SO_4$$

(Ross *et al.*, 1982).

The K form of jarosite is the most common, however, Na and hydronium (H_3O) forms have been reported in acid sulphate soils (Dent, 1986). The Na form, $NaFe_3(SO_4)_2(OH)_6$, is called natrojarosite.

Above pH 3.7, jarosite becomes metastable and eventually hydrolyzes to goethite:

$$KFe_3(SO_4)_2(OH)_6 \rightarrow 3FeOOH + K^+ + 3H^+ + 2SO_4^{2-}$$

(Dent, 1986).

Goethite can also form directly from reactions in solution during pyrite weathering (*i.e.*, jarosite does not form), shown as follows:

$$Fe^{2+} + SO_4^{2-} + \tfrac{1}{4}\, O_2 + {}^3\!/_2\, H_2O \rightarrow FeOOH + 2H^+ + SO_4^{2-}$$

(van Breemen, 1982).

Ultimately, most of the Fe from pyrite weathering forms ferric oxides, usually goethite (van Breemen, 1982).

High concentrations of dissolved aluminum (Al^{3+}) and silica (SiO_2) are other common characteristics of acid sulphate soils and groundwater. The extremely low pH levels (< 4; van Breemen and Buurman, 1998) cause dissolution of clay minerals, which results in release of Al^{3+} and SiO_2 to soil solution. The dissolved Al^{3+} further enhances

acidity. As pyrite weathering wanes and pH rises, Al^{3+} precipitates as basic aluminum sulphates (Dent, 1986). High concentrations of dissolved SiO_2 can lead to the formation of SiO_2 microfossils of plant remains (van Breemen, 1982), known as 'plant opal'.

Post-active acid sulphate soils are characterized by complete oxidation of all sulphides, and pH above 4 (Carson *et al.*, 1982). Sulphuric acid is no longer produced. Most of the sulphate washes away, except for that which precipitates with cations such as Ca^{2+}, K^+, and Al^{3+}. Most of the Fe released by pyrite weathering remains in the soil profile, most notably as goethite. In older, more developed acid sulphate soils, goethite often dehydrates to hematite, the more thermodynamically stable of the two minerals:

$$2FeOOH \rightarrow Fe_2O_3 + H_2O$$

(van Breemen and Buurman, 1998).

Complete hydrolyzation of jarosite to goethite and transformation of goethite to hematite may take centuries to occur. Thus, most post-active acid sulphate soils have a combination of these minerals present at once. Due to hydrolysis reactions and leaching, the pH of acid sulphate soils gradually increases (van Breemen and Buurman, 1998).

2.6.6. Arsenic in Boundary Soils

Arsenic is usually present in acid sulphate soils, as it readily substitutes for sulphur in the pyrite structure and can accumulate as a minor component. The As becomes released during pyrite weathering (Dudas, 1987), as discussed earlier. In the Boundary Soils, As concentrations were highest in the B and C horizons (up to 45 $\mu g\ g^{-1}$; Dudas, 1984), perhaps as a result of being mobilized and washed downward by water (Dudas *et al.*, 1988). Additionally, some As may have been translocated down into the soil profile with eluviated clays (Dudas, 1984). Arsenic concentrations were lower in the surface soils, presumably due to biological formation of volatile As compounds, like methylarsines (Dudas, 1984), and subsequent loss through diffusion.

Arsenic may accumulate in selenite and natrojarosite crystals (Dudas *et al.*, 1988), but was found to be most strongly associated with the iron oxides in the soil, with concentrations of up to 450 $\mu g\ As\ g^{-1}$ measured in iron oxide veinlets in the fractured (and oxygenated) shale below the B horizon (Dudas, 1987). Arsenic distribution and accumulation in these soils appears to be connected to the reactions and behaviour of the

pyrite-derived iron oxides, as they dissolve and precipitate in the soil system (Dudas, 1987). Iron oxides identified in the B horizon were goethite, hematite, and trace amounts of lepidocrocite (Dudas *et al.*, 1988).

3. MATERIALS AND METHODS

3.1. SITE LOCATION AND DESCRIPTION

Soil samples for this study were collected on September 9, 2000 from an area of Boundary Soils located approximately 60 km northwest of the town of Spirit River, Alberta (Figure 1), at Section 09, Township 82, Range 08, West of the 6th Meridian (Sec. 09-82-08 W6M). The area is part of the Low Boreal Mixedwood Ecoregion, which receives approximately 380 mm of precipitation annually. This ecoregion is located between aspen parkland and boreal forest and, thus, tends to have high wildlife diversity. The soils in the area tend to be nutrient-poor, resulting in sub-optimum agricultural production (Strong and Leggat, 1992).

The site selected for study was a typical Boundary Soil catena in the area, with a south-facing slope (11.5 ° angle at the west end, and 16 ° at the east end; Figure 2). At the time of sampling, aspen (*Populus tremuloides*), of relatively small diameter (from 6 to 14 cm), occurred as the main, but sparse, overstory species (Plate 1). Birch (*Betula papyrifera*) was less commonly present in the overstory. Alder (*Alnus* spp.), willow (*Salix* spp.), bearberry (*Arctostaphylos uva-ursi*), cranberry (*Vaccinium vitis-idaea*), rose (*Rosa acicularis*), and horsetail (*Equisetum* spp.) occurred as understory species at the bottom of the slope, in a depressional area. Little understory vegetation was present on upper and mid-slope positions (Plate 2).

Soil samples were collected from three transects (T1, T2, and T3) on the slope, at four positions (knoll, mid, toe, and depression) along each transect, and from distinct horizons (A, B1, B2, C) at each slope position (Figures 2 and 3), except for the depression, where only one B horizon was observed. Transects 1 and 2 were 9 m apart at the knoll top and 4.5 m apart in the depression. Transects 2 and 3 were 12 m apart at the knoll top and 2.5 m apart in the depression. Knoll and mid-slope sampling locations were 7, 11, and 12 m apart; mid and toe sampling locations were 6.5, 4.5, and 3.5 m apart; and toe and depression sampling locations were 4.5, 2.5, and 2.5 m apart in T1, T2, and T3, respectively. The upper groundwater zone was encountered at approximately 0.5 m below ground surface at the toe of the slope and at ground surface in the depression (Figures 2 and 3).

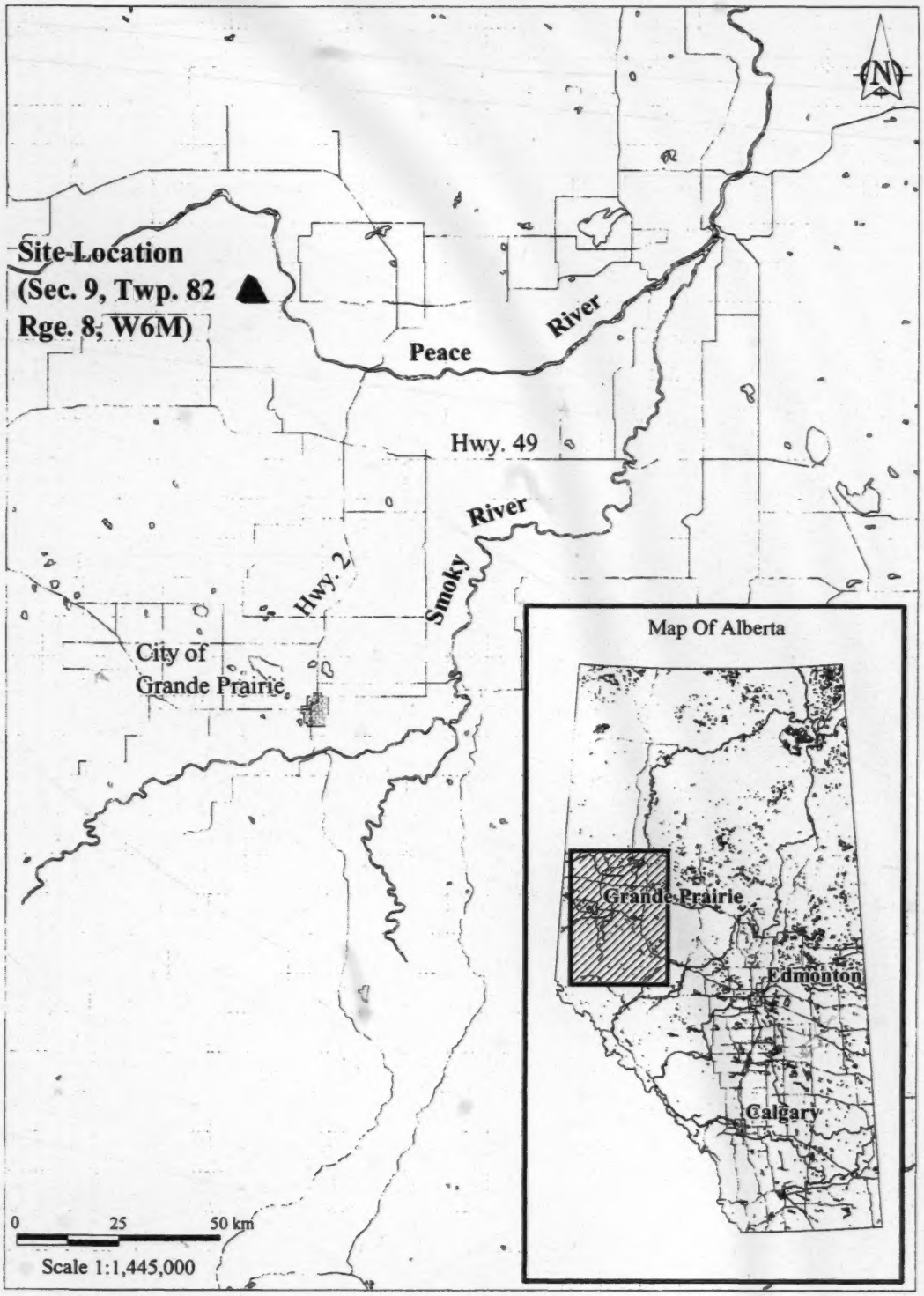

Figure 1. Site location

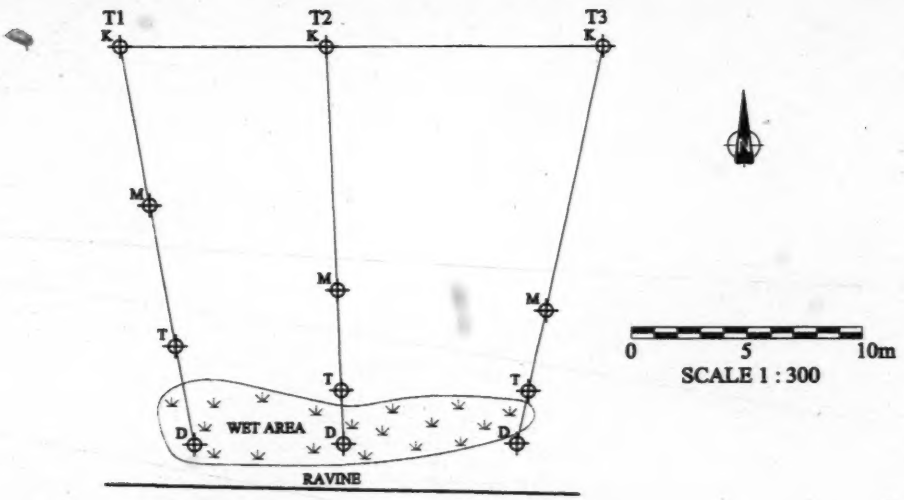

Figure 2: Planar view of Transects 1 to 3 and soil sampling locations (indicated by symbol).

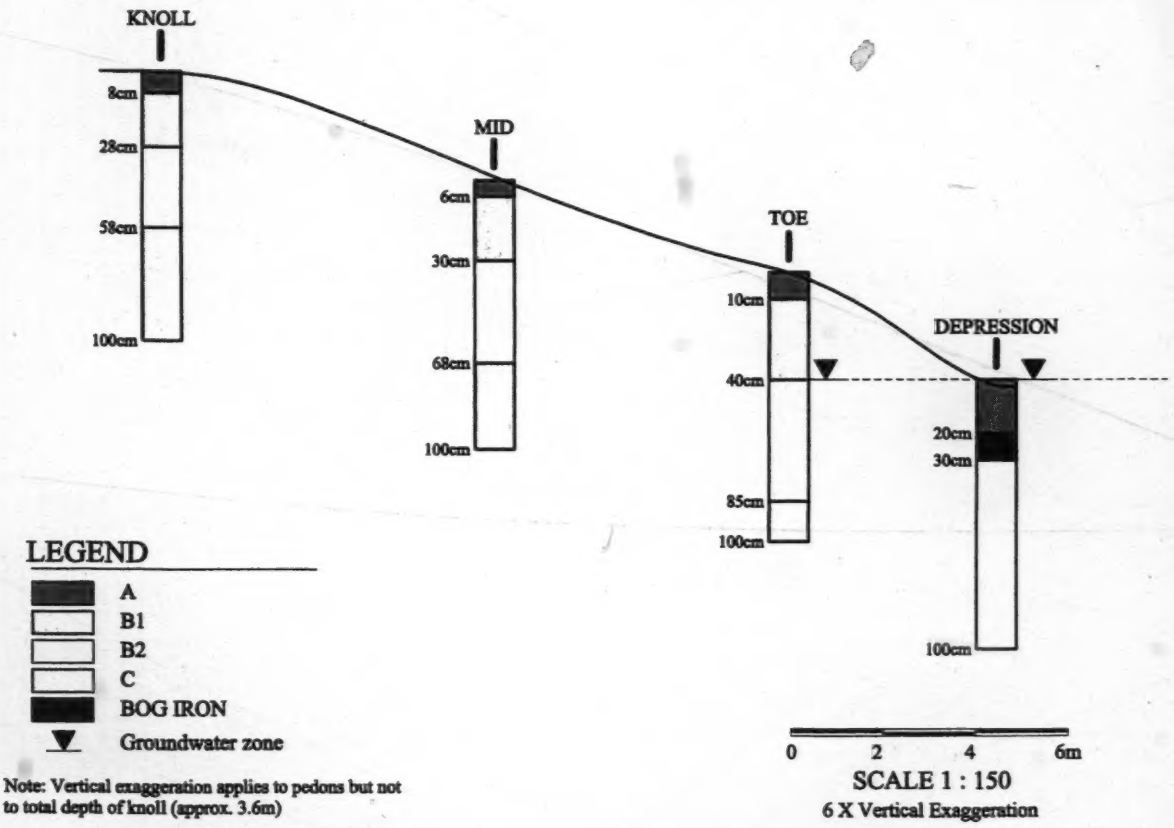

Figure 3: Cross-sectional view of Transect 1 soil sampling locations.

Plate 1. East view along knoll top.

Plate 2. View of Transect 1 from knoll top.

3.2. Sample Collection

3.2.1. Soil

Forty-five soil samples were collected from the site. Samples were placed in plastic Ziploc® bags and stored in coolers until they could be refrigerated, about 12 hours later. Soil profile depths were noted in the field; Munsell colour and soil descriptions were recorded in the laboratory and, therefore, do not include soil structure or horizon boundaries. A detailed soil description is included in Section 4.2.

3.2.2. Water

The soil pits dug in the depression/ravine area at the bottom of the slope filled with water. Three groundwater samples (one from each transect) were collected from these pits into plastic bottles. They were stored in coolers until they could be refrigerated, about 12 hours after collection. The samples were filtered and preserved in the laboratory prior to analysis.

3.3. Quantitative Analyses

3.3.1. Soil

Saturated Pastes

Measurements of redox potential (Eh), pH, and electrical conductivity (EC) were not obtained in the field; these parameters were determined in the laboratory on saturated pastes or saturated paste extracts (as appropriate) of each of the 45 samples, following the method of Rhoades (1982).

A sub-sample of moist (refrigerated) soil was weighed, then oven-dried for 24 hours to determine water content (Table A-1, Appendix). A large portion (approximately 1.5 L) of the refrigerated samples was air-dried, then ground to pass a 2 mm sieve. Saturated pastes were made by adding distilled, de-ionized water to an amount of ground soil (250 to 400 g) sufficient to yield an adequate-sized extract (10 to 20 mL). The pastes were sealed and left to equilibrate (at 25 °C and 1 atm) for six full days. Some samples absorbed all the water, rendering the pastes undersaturated; if necessary, more water was added on the fourth day to regain saturation. Prior to paste extraction, a sub-sample of the pastes was taken, weighed, and oven-dried for 24 hours to determine saturation per cent (Table A-1, Appendix).

The pastes were transferred to 250 mL, hard plastic Nalgene® centrifuge tubes and were centrifuged using an International Equipment Company® centrifuge at 380 *g* for 15 minutes. The supernatant was vacuum filtered using Whatman 7.0 cm, 42 (slow), ashless filters.

Redox Potential

Redox potential (Eh) was measured in each of the 45 soil samples. Redox potential is a measure of intensity of reduction-oxidation reactions (electron gaining and losing reactions, respectively) in a soil system. Redox potential is an important indicator of microbial activity, and can influence the speciation (and, thus, behaviour) of various elements. Immediately upon opening the pastes and before extraction, redox potential was measured by inserting a Cole-Parmer® probe directly into the paste and waiting for the reading to stabilize (usually five minutes) on the Cole-Parmer Digisense® digital pH/mV/ORP meter. The reading was recorded. Then the pastes were extracted, as described above, and the resulting extract was used to measure pH and electrical conductivity.

pH value

pH was measured by inserting the probe (same brand equipment as above) directly into the extract, waiting for the reading to stabilize, and recording the reading. The probe was standardized with pH 4 and 7 buffers prior to use. pH was also measured by 2:1 $CaCl_2$ method (Hendershot *et al.*, 1993). 20 mL of 0.01 M $CaCl_2$ solution was added to 10.0 g of dried and ground soil. The mixture was stirred periodically for 30 minutes, then left to sit for 60 minutes. pH was measured by inserting the probe directly into the mixture and recording the reading after it stabilized.

Electrical Conductivity

Electrical conductivity (EC) was measured on the saturation extract using a YSI Model 31 conductivity bridge. Prior to measuring EC on sample extracts, conductance was determined on standard 0.01 M KCl solution.

Total Elements

The concentrations of 21 elements [aluminum (Al), arsenic (As), bromine (Br), cerium (Ce), cobalt (Co), chromium (Cr), iron (Fe), hafnium (Hf), potassium (K), lanthanum (La), manganese (Mn), sodium (Na), rubidium (Rb), antimony (Sb), scandium

(Sc), samarium (Sm), thorium (Th), titanium (Ti), uranium (U), vanadium (V), and zinc (Zn)] were measured in each of the 45 bulk soil samples using instrumental neutron activation analysis (INAA). Samples were analyzed at the SLOWPOKE (Safe Low Power Kritical Experiment) II Nuclear Reactor at the University of Alberta. Soil samples, weighing between 180 and 500 mg, were accurately weighed into nitric-acid washed, 0.75 mL reactor-grade polyethylene vials, hermetically sealed, and individually placed in 7 mL polyethylene vials with a spacer for neutron irradiation. To determine those elements which produce short-lived radionuclides upon thermal neutron irradiation, each sample was individually irradiated for 240 s in an inner site of the reactor at a nominal thermal neutron flux of 2×10^{10} n cm^{-2} s^{-1}. Following irradiation, the inner 0.75 mL vial containing the soil sample was removed from the 7 mL irradiation vial (to avoid any possible external contamination) and was counted, following a decay period of approximately 12 minutes for 360 s live-time. Counting was performed at a sample-to-detector distance of 6 cm using a 20 % efficiency hyperpure Ge detector with a full width half maximum (FWHM) resolution of 1.85 keV for the 1332 keV full energy peak of ^{60}Co. Spectra were collected using an E&G ORTEC digital spectrometer.

Element quantification was performed by the semi-absolute comparator method of NAA (Bergerioux *et al.*, 1979) and standard reference materials of known composition were analyzed under the same conditions as the soil samples for QA/QC. The standards used were National Institute of Standards and Technology (NIST) 1645 (river sediment; Gladney *et al.*, 1987), NIST 1633a (flyash; Gladney *et al.*, 1987), NIST 1646 (estuarine sediment; Gladney *et al.*, 1987), SCo-1 [Cody Shale, United States Geological Survey (USGS); Gladney and Roelandts, 1988], and SO-2 [Podzolic B horizon soil; Canadian Centre for Mineral and Energy Technology (CANMET); Bowman *et al.*, 1979]. Table A-5 (Appendix) shows the standards that were analyzed for each element, associated uncertainties for the analysis, and consensus values and associated uncertainties for the standards.

Table 1 lists the specific radionuclides, their half-lives, and principal gamma-ray(s) used for elemental quantification following the short irradiation.

Table 1. Nuclear data for short-lived radionuclide analysis.

Element	Radio-Nuclide	Nuclear Reaction	Half-life	Principal γ-ray(s) (keV)
Al	^{28}Al	^{27}Al(n,γ)^{28}Al	2.24 min	1778.7
Ti	^{51}Ti	^{50}Ti(n,γ)^{51}Ti	5.80 min	320.1
V	^{52}V	^{51}V(n,γ)^{52}V	3.75 min	1434.0
Na	^{24}Na	^{23}Na(n,γ)^{24}Na	14.96 hrs	1368.5
Mn	^{56}Mn	^{55}Mn(n,γ)^{56}Mn	2.58 hrs	846.6, 1811.2

Following a suitable decay, samples (a maximum of four per 7 mL polyethylene irradiation vial) were packed for neutron irradiation and determination of those elements which produce long-lived radionuclides upon thermal neutron irradiation. Batches of samples were irradiated for 4 hrs in an inner site of the reactor at a nominal thermal neutron flux of 5 x 10^{11} n cm^{-2} s^{-1}. Following a decay period of approximately 6 days, the samples were individually counted for a minimum of 3600 s using, in the early stages of the work, a 20 % hyperpure Ge detector at a sample-to-detector distance of 3 cm (later, a 41 % hyperpure Ge detector was used). For both detectors, the FWHM resolution was better than 1.9 keV for the 1332 keV full energy peak of ^{60}Co. Spectra were collected using APTEC PC-based MCArds. In some instances, samples were recounted following a decay period of approximately 21 d at a sample-to-detector counting geometry of 1 cm.

As with the short-irradiation analyses, elements were quantified using the semi-absolute method of NAA (Bergerioux *et al.*, 1979). Relevant nuclear data on the longer-lived radionuclides analyzed in this study are listed in Table 2.

Table 2. Nuclear data for long-lived radionuclide analysis.

Element	Radionuclide	Nuclear Reaction	Half-life	Principal γ-ray(s) (keV)
As	^{76}As	$^{75}As(n,\gamma)^{76}As$	26.32 h	559.1
Fe	^{59}Fe	$^{58}Fe(n,\gamma)^{59}Fe$	44.496 d	1099.2, 1291.6
La	^{140}La	$^{139}La(n,\gamma)^{140}La$	40.27 h	328.8, 487.0, 1596.5
Na	^{24}Na	$^{23}Na(n,\gamma)^{24}Na$	14.96 hrs	1368.5
Cr	^{51}Cr	$^{50}Cr(n,\gamma)^{51}Cr$	27.70 d	320.1
Sm	^{153}Sm	$^{152}Sm(n,\gamma)^{153}Sm$	46.7 h	103.2
Ce	^{141}Ce	$^{140}Ce(n,\gamma)^{141}Ce$	32.50 d	145.4
U	^{239}Np	$^{239}U(n,\gamma)^{239}U \rightarrow ^{239}Np$	2.355 d	228.1, 277.6
Th	^{233}Pa	$^{232}Th(n,\gamma)^{233}Th \rightarrow ^{233}Pa$	27.0 d	312.0
Hf	^{181}Hf	$^{180}Hf(n,\gamma)^{181}Hf$	42.39 d	482.2
Sb	^{122}Sb	$^{121}Sb(n,\gamma)^{122}Sb$	2.70 d	564.1
Co	^{60}Co	$^{59}Co(n,\gamma)^{60}Co$	5.27 y	1173.2, 1332.5
Zn	^{65}Zn	$^{64}Zn(n,\gamma)^{65}Zn$	243.9 d	1115.5
Br	^{82}Br	$^{81}Br(n,\gamma)^{82}Br$	35.3 h	619.1, 776.5
Rb	^{86}Rb	$^{85}Rb(n,\gamma)^{86}Rb$	18.66 d	1076.6
Sc	^{46}Sc	$^{46}Sc(n,\gamma)^{46}Sc$	83.81 d	889.3, 1120.5
K	^{42}K	$^{41}K(n,\gamma)^{42}K$	12.36 h	1524.6

Since As was originally the main focus of the study, a detection limit for As has been determined based on the criterion of Currie (1968). Based on the four hour irradiation at 5 x 10^{11} n cm^{-2} s^{-1}, followed by a five day decay period, and a one hour count at a sample-to-detector geometry of 3 cm using a nominally 20 % hyperpure Ge detector, the average detection limit for As in four samples (PB-17, -18, -27, and -28; Table A-4, Appendix) was 0.71 μg g^{-1} for a 356 mg sample. This detection limit was sufficient for the study, given that the lowest arsenic concentration in the samples analyzed was 10.0 μg g^{-1} (Table A-4, Appendix).

3.3.2. Water

Ten total elements [aluminum (Al), arsenic (As), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), potassium (K), and selenium (Se), sodium (Na)] were analyzed in water samples by inductively coupled plasma – mass spectrometry (ICP-MS) at the Alberta Research Council in Vegreville, Alberta. All measurements were performed with a Perkin-Elmer SCIEX (Thornhill, Ontario, Canada) Elan Model 5000 ICP quadruple mass spectrometer. Samples were filtered in the laboratory with AdvanTec MFS Inc. 47 mm cellulose acetate membrane filters with 0.45 μm-sized mesh, and preserved with 10 % HNO_3. Eh, EC, and pH were measured on the groundwater samples with the same probes used for the soil measurements (Section 3.3.1).

3.4. Qualitative Soil Analyses

3.4.1. Plant Opal Morphology

Two sub-samples of plant opal were prepared for scanning electron microscopy: one small (approximately 1 cm^3) aggregate of opal and some opal "dust" that had accumulated in the bottom of the sample pan. The samples were coated in gold prior to examination. Scanning electron microscopy was used to examine the morphology of the opal at the micron (10^{-6} m) scale. Images were obtained using a JEOL model JSM6301FXV scanning electron microscope equipped with an energy-dispersive x-ray analyzer (EDX) for qualitative elemental analysis.

3.4.2. Iron Oxide Identification

X-ray diffraction was used to identify the types of minerals present in the Fe-rich layer in the depression at the bottom of the slope. Air-dried samples of bulk soil were ground to fine powder using an agate mortar and pestle. Samples were prepared as random powder mounts, then analyzed for diffraction behaviour using a Philips PW1710 Diffractometer equipped with a curved crystal monochrometer. Cobalt radiation generated at 25 mA and 50 kV was used for the analysis.

4. RESULTS AND DISCUSSION

4.1. LITERATURE DATA

Various parameters of the Boundary Soils have been measured and reported by other researchers and, therefore, were not determined during this study. Some of these data have been compiled (see Table A-2, Appendix) and are summarized below. Note that Bulmer's (1987) study was similar to the present one in that soil samples were collected from discrete horizons at four points (upper, mid, lower-mid, and lower) along a bedrock outcrop of Boundary Soils. Therefore, data from Bulmer can be considered surrogate data for the present study.

Goethite (α-FeOOH) and hematite (α-Fe_2O_3) were generally found to be the dominant iron oxides present in the soil profiles, particularly in the B horizons. Traces of jarosite usually occurred below the A horizon, and natrojarosite showed a stronger presence in the lower solum, particularly in lower C horizons (Pawluk and Dudas, 1978; Bulmer, 1987; Dudas *et al.*, 1988). Phyllosilicates consisted mainly of mica (more predominant in the lower solum) and kaolinite (more predominant in the upper horizons; Pawluk and Dudas, 1978; Bulmer, 1987; Dudas *et al.*, 1988). Smectites were observed by Dudas *et al.* (1988) in A, B, and C horizons. Extractable iron oxides data showed less dithionite-extractable Fe (all extractable secondary iron oxides) in lower slope positions (ranging from 1.56 to 4.42 %) relative to upper slope positions (ranging from 3.18 to 6.92 %; Bulmer, 1987). pH was low (ranging from 3.1 to 4.0) and generally decreased with depth into the solum (Bulmer, 1987). Base saturation was low (ranging from 1.7 to 12.7 % in B, BC, and C horizons) relative to cation exchange capacity (average 20.4 cmol(+) kg^{-1}), except in the A horizons along the slope (average base saturation of 31.1 %; Bulmer, 1987). Organic C ranged from 0.5 % in the B horizon, to over 3 % in the A horizon (Pawluk and Dudas, 1978; Bulmer, 1987). B and C horizons were clay-rich and depleted in sand, typical of soils derived from shale (Bulmer, 1987). They fall within the 'clay' textural class (Brady and Weil, 1996). B horizons were higher in clay (59 to 69 %; Bulmer 1987) than C horizons (54 to 57 %; Bulmer, 1987; Table A-2, Appendix).

Bulk density of the A horizons (0.85 to 0.91 Mg m^{-3}; Bulmer, 1987) was within the range for uncultivated loamy A horizons (Brady and Weil, 1996); bulk density of the

B and C horizons (1.15 to 1.41 Mg m^{-3}; Bulmer, 1987) was within the range for clay-rich soils (Brady and Weil, 1996). Arsenic concentrations were generally elevated in the B and C horizons (30 to 40 μg g^{-1}; Dudas, 1984; Dudas, 1987) relative to most soils, and were even higher in the fine clay fraction (up to 54 μg g^{-1}; Dudas, 1987) and iron oxide veinlets (up to 450 μg g^{-1}; Dudas, 1984; Bulmer, 1987; Dudas, 1987; Dudas *et al.*, 1988). Arsenic was relatively low in the A horizons (around 7 to 8 μg g^{-1}; Dudas, 1984; Dudas, 1987; Table A-2, Appendix).

4.2. Soil Description

Descriptions of soil samples collected for the current study were recorded in the laboratory and are presented in Table A-3 (Appendix).

Soil in the A horizon (Ah) along the slope generally consisted of dry to moist, dark brown to black or grayish brown silty clay with abundant semi-decomposed organic matter (*e.g.*, wood and leaves) and roots. The surface horizon in the depressional area was called an Om/Ah horizon on account of the large proportion of organic matter present in the surface horizon of that area.

At most slope positions, the upper portion of the B horizon exhibited different characteristics (*e.g.*, colour, root abundance) than the lower portion. These portions were, therefore, sampled, described, and analyzed separately. They were designated B1 and B2, respectively.

The B1 horizons along the slope were classified as Bfj (knoll and mid-slope positions) or Bg (toe) horizons. Manual texturing indicated an increase in clay content compared to the A horizon. B1 horizons were generally dry to moist, brown to dark brown silty clay to clay with many roots. In the depressional area, the term "Bog Iron" was given to the B1 horizon, as it was predominantly red in colour, organic matter-rich, and saturated.

The B2 horizons along the slope were also Bfj (knoll and mid-slope positions) or Bg (toe) horizons. They were generally strong brown to dark yellowish brown to greenish grey (toe) in colour, dry to moist clay to hard clay with few roots. Yellow stones were observed in two of the B2 horizon samples. No distinct B2 horizon was observed in the depression.

The C horizons were classified as Cg horizons in the toe and depression slope positions. They were generally dark grey to greenish grey, clay to hard clay, forming large, hard aggregates. The samples were generally dry to moist, except in some toe and depressional samples, which were wet.

Proper pedological descriptions were not recorded during this study. Therefore, complete profile descriptions of upper, mid-, lower-mid, and lower slope positions of the Boundary Soils from Bulmer (1987) are provided in Tables 3 to 6.

Table 3. Upper slope Boundary Soil profile description (Bulmer, 1987).

Horizon	Depth (cm)	Description
L	2-0	Undecomposed leaf litter.
Ahe	0-4	Yellowish brown (10YR 5/6m); silty clay; strong, fine granular; friable; abundant, fine and very fine, random roots; clear, smooth boundary.
Btfj1	4-26	Brown (7.5YR 4/6m); heavy clay; strong, fine subangular blocky; firm; abundant, medium, oblique to horizontal roots; gradual, wavy boundary.
Btfj2	26-43	Reddish brown (5YR 4/6m); heavy clay; strong, fine subangular blocky; friable; abundant, medium, horizontal roots; abrupt, wavy boundary.
BC	43-58	Dark grayish yellow (2.5Y 5/2m); silty clay; few, fine, prominent, bright reddish brown (5YR 5/6) mottles; weak to moderate, medium subangular blocky; firm; few, fine roots; gradual, wavy boundary.
C1	58-75	Yellowish grey (2.5Y 5/1m); silty clay; massive; firm; no roots; gradual, wavy boundary.
C2	75-95	Yellowish grey (2.5Y 4/1m); silty clay; massive; firm; no roots; clear, wavy boundary.
C3	95-110	Yellowish grey (2.5Y 4/1m); silty clay; common, medium, prominent, pale yellow (5Y 8/4) soft powdery concretions and lamellae; massive; firm; no roots.

Table 4. Mid-slope Boundary Soil profile description (Bulmer, 1987).

Horizon	Depth (cm)	Description
L	2-0	Undecomposed leaf litter.
Ahe	0-4	Brown (7.5YR 4/4m); heavy clay; strong, fine granular; friable; abundant, very fine and fine, random roots; clear, smooth boundary.
Btfj1	4-18	Brown (7.5YR 4/6m); heavy clay; strong, fine subangular blocky; firm; abundant medium, few coarse, horizontal roots; gradual, wavy boundary.
Btfj2	18-36	Reddish brown (5YR 4/6m); heavy clay; strong, fine subangular blocky; firm; abundant, medium, horizontal roots; abrupt, wavy boundary.
BC	36-55	Yellowish grey (2.5Y 5/1m); silty clay; many, medium, prominent, reddish brown (5YR 4/6) mottles; weak, fine subangular blocky; firm; plentiful, medium, oblique roots; gradual, wavy boundary.
C1	55-75	Yellowish grey (2.5Y 4/1m); silty clay; common, medium, prominent, yellowish brown (10YR 5/6) mottles; common, medium, prominent, pale yellow (2.5Y 8/4) soft powdery concretions and lamellae; massive; firm; no roots; diffuse boundary.
C2	75-95	Yellowish grey (2.5Y 5/1m); silty clay; common, medium, prominent, bright brown (7.5YR 5/6) mottles; common, medium, prominent, pale yellow (2.5Y 8/4) soft powdery concretions and lamellae; massive; firm; no roots; diffuse boundary.
C3	95-105	Yellowish grey (2.5Y 4/1m); silty clay; common, medium, prominent, orange (7.5YR 6/6) mottles; common, medium, prominent, pale yellow (2.5Y 8/4) soft powdery concretions and lamellae; massive; firm; no roots; diffuse boundary.

Table 5. Lower-mid slope Boundary Soil profile description (Bulmer, 1987).

Horizon	Depth (cm)	Description
L	5-0	Fibrous leaf litter.
Ahe	0-5	Brown (7.5YR 4/4m); silty clay; strong, fine granular; very friable; abundant, very fine and fine, random roots; clear, smooth boundary.
Btfj1	5-15	Brown (7.5YR 4/4m); heavy clay; strong, fine subangular blocky; friable; abundant, medium, oblique roots; clear, wavy boundary.
Btfj2	15-30	Brown (7.5YR 4/6m); heavy clay; strong, fine subangular blocky; firm; abundant, medium and coarse, oblique roots; clear, wavy boundary.
Btfj3	30-50	Reddish brown (5YR 4/6m); heavy clay; strong, fine and medium subangular blocky; firm; abundant, medium, oblique roots; clear, wavy boundary.
BC	50-65	Yellowish grey (2.5Y 5/1m); heavy clay; many, medium, prominent, brown (7.5YR 4/6) mottles; weak, fine subangular blocky; firm; plentiful medium, few coarse, oblique roots; clear, wavy boundary.
C1	65-80	Yellowish grey (2.5Y 5/1m); silty clay; few, medium, prominent, dull brown (7.5YR 5/4) mottles; amorphous; firm; few, medium, oblique roots; gradual, wavy boundary.
C2	80-105	Yellowish grey (2.5Y 4/1m); silty clay; few, medium, prominent, pale yellow (2.5Y 8/4) soft powdery concretions and lamellae; amorphous; firm; no roots.

Table 6. Lower slope Boundary Soil profile description (Bulmer, 1987).

Horizon	Depth (cm)	Description
LFH	7-0	Humified and fibrous leaf litter.
IAhe	0-6	Dark brown (7.5YR 3/4m); silty clay loam; moderate, medium granular; very friable; plentiful, fine, random roots; clear, smooth boundary.
IBtfj1	6-16	Brown (7.5YR 4/4m); silty clay loam; moderate, medium granular; very friable; abundant, medium, oblique roots; diffuse, wavy boundary.
IBtfj2	16-27	Brown (7.5YR 4/4m); silty clay; strong, fine subangular blocky; friable; abundant, medium, oblique roots; clear, wavy boundary.
IIBtfj	27-40	Brown (7.5YR 4/4m); silty clay; strong, fine, subangular blocky; firm; abundant, medium, oblique roots; abrupt, wavy boundary.
IIBC	40-60	Dull yellowish brown (10YR 5/3m); silty clay; moderate, medium subangular blocky; firm; abundant, medium, oblique roots; clear, wavy boundary.
IIC1	60-83	Dark grayish yellow (2.5Y 4/2m); silty clay; massive; firm; few, medium, oblique roots; clear, wavy boundary.
IIC2	83-100	Yellowish grey (2.5Y 4/1); silty clay; common, fine, prominent pale yellow (2.5Y 8/4); soft powdery concretions and lamellae; massive; firm; few, fine, oblique roots.

4.3. Main Chemical Parameters

4.3.1. Redox Potential

Eh was measured in the laboratory on saturated pastes of the samples; therefore, true redox conditions in the field at the time of sampling are unknown. Regardless of the method of measurement, Eh is highly variable and difficult to measure. When a soil is re-wet after drying, it will display different behaviour than a continuously wet soil (Bartlett, 1986). Redox potential measurements can be useful, but their limitations must be recognized.

Redox potential was lowest in the A horizon samples, with values ranging from -201 to 470 mV, and an average of 297 mV (Figure 4; Table A-1, Appendix). Microbial population size in surface soils is typically higher than of other horizons due to a greater

amount of organic matter. Microbial activity was likely high in the saturated pastes during the equilibration period, resulting in depleted oxygen and low redox potential. Redox in the B1 horizon ranged from -208 to 582 mV; the range in the B2 horizon was 539 to 637 mV. Redox potential increased with depth into the profile, and was highest in the C horizon (values ranging from 592 to 672 mV). Diffusion of air into the C horizon is expected to be minimal, particularly in fine-textured soils; the acidic conditions maintain the Eh at relatively high voltage. Clark (1966) reported high redox potentials in water where pyrite oxidation was occurring, ranging from approximately 600 to 800 mV.

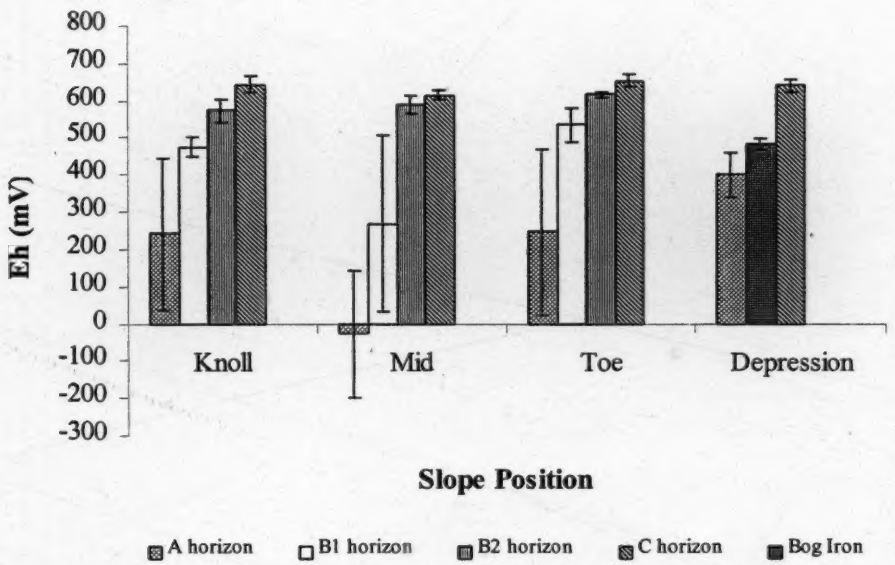

Figure 4. Average redox potential in soil horizons along the slope.

[Note: each column on the graph is an average of three values (one from each sampling transect). Error bars represent standard error of the mean. All column graphs in this document were prepared in this fashion.]

Redox potential was fairly constant down the slope in horizons B1, B2, and C. In the A horizon, Eh increased down slope; the lower pH in the depression (Section 4.3.2) is likely buffering the Eh.

4.3.2. pH

In general, pH for all samples analyzed was low (generally between 3 and 5). The average pH was 4.23. Low pH is typical of acid sulphate soils (Section 2.6.5), as they contain sulphuric acid from the weathering of pyrite.

Saturated paste extract pH data indicated that pH generally decreases down the slope (Figure 5; Table A-1, Appendix). This indicates that H^+ and Al^{3+} might be migrating down slope and are depleted at the knoll relative to the depression. pH ranged from 3.17 (toe Transect 1, C horizon) to 7.15 (mid-slope Transect 2, C horizon). Of the horizons, the C horizon generally exhibited the lowest pH (average 4.12). Although not obvious on Figure 5, the B2 horizon had the highest average pH (4.35).

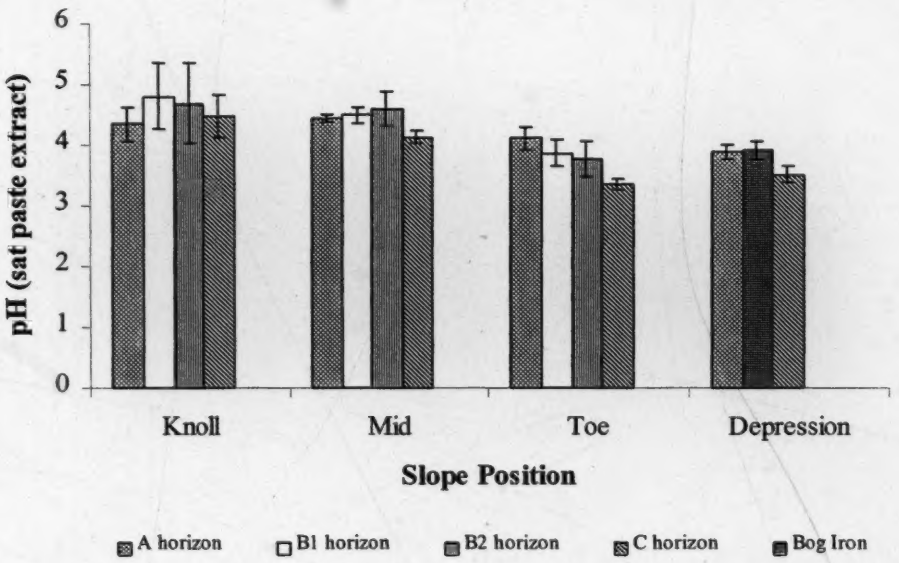

Figure 5. Average pH (saturated paste extract) in soil horizons along the slope.

Analyzing pH of soil in dilute $CaCl_2$ generally yielded pH values lower than by saturated paste extract, with an average of 3.52. Values ranged from 3.17 (toe Transect 1, C horizon) to 4.04 (mid-slope Transect 3, A horizon; Figure 6; Table A-1, Appendix). Lower pH values are a result of Ca^{2+} in the added $CaCl_2$ binding to the cation exchange complex and displacing H^+ and Al^{3+} ions into solution (Brady and Weil, 1996).

pH did not vary greatly between slope positions (Figure 6). A more distinct trend was observed within the solum, with pH values lowest in the C horizon (average 3.30) and highest in the A horizon (average 3.71). Bulmer (1987) also observed lower pH deeper in the solum. However, Bulmer (1987) also reported lower base saturation in the B and C horizons than in the A horizon.

The pH of water associated with active acid sulphate soils has been reported at 1.5 to 3.8 (Clark, 1966); pH of oxidizing pyritic mud was 1.8 to 4 (as reported in Bloomfield and Coulter, 1973), and cat clays oxidizing for six years had pH values of 3.0 to 3.5 (as reported in Bloomfield and Coulter, 1973). The pH range of Podzolic soils of southern Quebec was 4.47 to 4.75 (Courchesne and Hendershot, 1989). Thus, the pH of the Boundary Soils is within the range expected for post-active acid sulphate soils (slightly higher than that of active acid sulphate material).

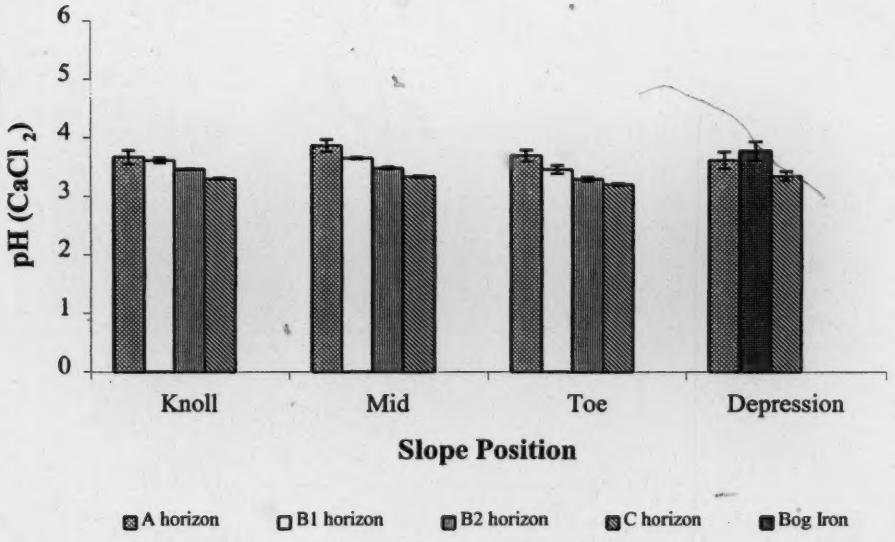

Figure 6. Average pH (by $CaCl_2$) in soil horizons along the slope.

4.3.3. Electrical Conductivity

Electrical conductivity (EC) values exhibited a clear trend down slope, with EC increasing from knoll to depression (Figure 7; Table A-1, Appendix). Average EC values ranged from 0.078 dS m^{-1} (knoll Transect 3, B2 horizon) to 2.05 dS m^{-1} (depression Transect 3, Om/Ah horizon). These results are consistent with down slope movement of soluble ions. There was no apparent trend in EC values with solum depth; the A horizon had the highest EC on average (0.796 dS m^{-1}) and the B2 horizon had the lowest EC on average (0.516 dS m^{-1}).

Clark (1966) reports ionic strength of 0.3 mol L^{-1} (approximately 23 dS m^{-1}) to be typical of mine water, and Bloomfield and Coulter (1973) discuss specific conductance values of greater than 10 dS m^{-1} for dried, oxidized, pyritic soils. Relative to these values, the Boundary Soils studied have low conductance, perhaps due to their post-active stage (many constituents would have been dissolved and transported during active oxidation).

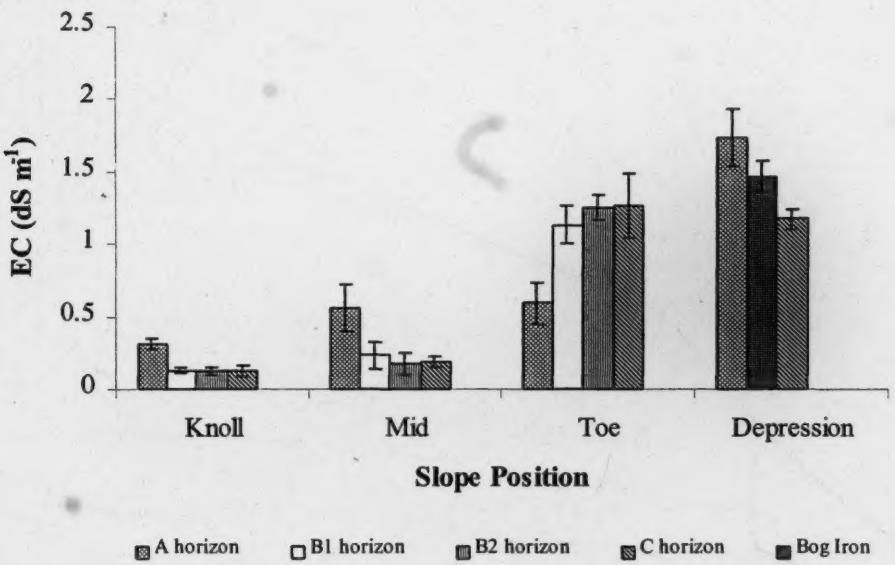

Figure 7. Average electrical conductivity values in soil horizons along the slope.

4.4. TOTAL ELEMENTS

4.4.1. General Observations

Each of the 45 soil samples collected for this study was analyzed for total concentrations of 21 elements. Originally, only As and Fe concentrations were to be determined; therefore, analysis conditions were optimized for As. It was later decided to obtain concentration data for other elements that activate well by NAA, to help elucidate the arsenic geochemistry in these soils. Elemental results are presented in Table A-4 (Appendix), along with analytical uncertainties for each value. Uncertainties were generally low (< 1 %) for Al, As, La, Sc, and Sm, as these elements activate particularly well compared to some others, such as Zn and Rb (with measurement uncertainties around 10 %).

Many elements showed fairly uniform concentrations both vertically and laterally, except in the Bog Iron and/or Om/Ah samples in the depression, where their concentrations either increased dramatically or were considerably depleted. Generally, the following was observed:

- Fe, As, Sb had highest concentrations in Bog Iron samples
- K, Al, La had lowest concentrations in Bog Iron samples
- Br, U, Sm, Sc had highest concentrations in Om/Ah and Bog Iron samples
- Na, Hf, Rb, Ti, V had lowest concentrations in Om/Ah and Bog Iron samples
- Ce, Cr, Th, Zn did not clearly increase or decrease down slope.

The remaining two elements (Co and Mn) did not exhibit any of the above trends. The lowest Co concentrations were in all samples of the depression (A, B, and C horizons); Mn was most concentrated in the A horizon at mid slope.

The Bog Iron and Om/Ah layers in the depression clearly formed in a different chemical environment than the other soil horizons studied as evidenced by the unusual concentrations exhibited by the various elements in these layers. Consequently, in some of the following discussions and statistical analyses, the data from these two layers have been excluded.

4.4.2. Boundary Soil Geochemistry and Comparisons

Concentrations of total elements in the C horizon samples of the current study were averaged and compared to those obtained by other researchers for different Alberta soils and to crustal abundance (Table A-6, Appendix). Bulmer's (1987) element data are from the parent material of the Boundary Soils; Warren's (1991) data are from calcareous till parent material of central Alberta; and Dudas and Pawluk's (1980) data are from a Ck2 horizon of a typical central Alberta Grey Luvisol which developed on glacial till. The majority of data are for trace elements, however, data for some major and minor elements were also determined and are included. All data were obtained by neutron activation analysis, except for those of Dudas and Pawluk (1980), who used a colorimetric method (Small and McCants, 1961) to determine As, and graphite furnace atomic absorption (GFAA) for Zn and Co determination.

Bulmer's data indicated that average Br, Co, and Mn concentrations (0.7, 3.5, and 23.8 $\mu g\ g^{-1}$, respectively) in the parent material of the Boundary Soils were particularly low relative to crustal abundances (6, 20, and 850 $\mu g\ g^{-1}$, respectively) and to other Alberta soils. Of particular note is the very low Mn content of the Boundary parent material. Manganese mobility with decreasing pH (to 2.7) has been observed (Fajtl *et al.*, 2001). Cobalt has been reported to be extensively leached from acid sulphate soils of western Finland (Astrom, 2001). Similarly, in an experimental study, high proportions of Co and Mn were released from oxidized sulphide-bearing, fine-grained sediments and became concentrated in the water phase (Astrom, 1998). Cobalt concentrations of 6.0 and 9.9 $\mu g\ g^{-1}$ soil were observed by Warren (1991) and Dudas and Pawluk (1980), respectively; 360 μg Mn g^{-1} soil was reported by Warren (1991). Analytical results from the current study indicated the same three elements are depleted (average 2.15 μg Br g^{-1}, 3.8 μg Co g^{-1}, and 38.7 μg Mn g^{-1}), as well as Na (average 2,600 $\mu g\ g^{-1}$ versus 6,600 $\mu g\ g^{-1}$ crustal abundance) relative to crustal abundances and other Alberta soils. Manganese and Co values are comparable between Bulmer and the current study; however, Br levels reported by Bulmer are significantly depleted (average 0.7 $\mu g\ g^{-1}$ in C horizon) relative to the present study (average 2.15 $\mu g\ g^{-1}$ in C horizon).

Bulmer reported enrichment of As and V (36.5 and 240 μg g^{-1}, respectively) versus crustal abundances of these elements (6.6 and 130 μg g^{-1}. The present study confirmed the enrichment of As and V reported by Bulmer with averages of 38.5 and 278 μg g^{-1}, respectively. Additionally, both studies found Ce was enriched (average 81.8 μg g^{-1}, current study; 71 μg g^{-1}, Bulmer) relative to crustal abundance (50 μg g^{-1}).

Iron was enriched in the current study (average 61,200 μg g^{-1}) relative to Bulmer (48,000 μg g^{-1}), Astrom (1998) for sulphide-bearing, fine-grained sediments (50,000 μg g^{-1}), and crustal abundance for shales (47,000 μg g^{-1}). The higher average Fe concentration reported in this study versus that reported by Bulmer (1987) can be attributed to the inclusion of the Fe-rich Bog Iron layer in this study, discussed in detail in Section 4.6.

Aluminum and Ti concentrations in the current study (average 82,400 and 4,530 μg g^{-1}, respectively) and in Bulmer's investigation (80,000 and 4,075 μg g^{-1}, respectively) are in very good agreement and are around the levels expected in shale (80,000 and 4,500 μg g^{-1} crustal abundance, respectively).

Astrom (1998) reported a median Cr concentration of 64 μg g^{-1}, which is approximately half of that found in the C horizon in the depression (average 120 μg g^{-1}).

Not surprisingly, many trace element concentrations determined by Warren (1991) for a soil developed from a calcareous till were lower than those from Bulmer's and the current study. Arsenic, Ce, Cr, La, Rb, Sc, Sm, Th, U, V and Zn are all enriched in the clay-rich Boundary Soils compared to Warren's calcareous till parent material. These elements are known to be associated with argillaceous deposits (Kabata-Pendias, 2001). Hafnium and Sb concentrations did not vary greatly between the three studies. Concentrations of Co and Mn were higher in Warren's study than in Bulmer's or the current study, although both of these elements were still lower than crustal abundance values. Dudas and Pawluk's study of a Grey Luvisol only included the three trace elements As, Zn, and Co. Arsenic and Zn were depleted in the Luvisol relative to the Boundary Soils, while Co was enriched. Zinc has been observed to increase in mobility with decreasing pH (to 2.7; Fajtl *et al.*, 2001).

Bloomfield and Coulter (1973) mention that clays of marine origin often have high levels of K (12,000 to 17,000 μg g^{-1}). The average K concentration in the C horizons of the soils studied was 25,300 μg g^{-1} (Table A-6). Potassium is discussed more extensively in Section 4.4.5.

In summary, elemental concentrations in the Boundary Soils were generally within expected ranges for soils developed on shale parent material. Exceptions were Br, Co, and Mn, which were depleted in the Boundary Soils relative to other Alberta soils; and As, V, and Ce, which were enriched in the Boundary Soils relative to other Alberta soils.

4.4.3. Elemental Correlations

Pearson correlation coefficients were determined on the Boundary Soil samples using SAS statistical software (The SAS System for Windows V8; Copyright © 1999-2000 by SAS Institute, Inc., Cary, NC, USA). A correlation matrix for the complete NAA data set is shown in Table 7. Since markedly different element concentrations were often observed in the Bog Iron and Om/Ah layers of the depression, correlations were also determined excluding the samples from these layers (Tables 8 and 9). Indeed, several elements (*e.g.*, As, Sb, and Mn) had a greater number of significant correlations in the absence of the Bog Iron and Om/Ah samples. Arsenic was significantly correlated with eight elements (Al, Cr, K, La, Rb, Sb, Ti, V) with the Bog Iron samples excluded, and only one (Sb) with the full data set. Manganese was significantly correlated (negatively) with five elements (Ce, Cr, K, La, Th) in the absence of the Bog Iron samples, and only one (Th) with the full data set. The Bog Iron and Om/Ah samples are outliers in the data and mask associations and trends that are present. Thus, for some parts of this discussion, data will be viewed without these samples. Correlation coefficients could not be determined on Bog Iron samples alone, as the small sample number (n = 3) resulted in low t values and, therefore, no significant correlation coefficients for any of the element pairs.

Table 7. Correlation matrix of elemental data for all samples.

Element																					
Sm	---																				
Ce	0.18	---																			
U	0.74	0.11	---																		
Th	0.13	0.74	0.30	---																	
Hf	-0.44	0.48	-0.40	0.31	---																
As	-0.20	0.26	-0.27	0.44	-0.02	---															
Sb	-0.07	0.25	-0.14	0.51	-0.04	0.93	---														
Fe	0.32	-0.28	0.29	0.05	-0.57	0.48	0.62	---													
Cr	-0.35	0.69	-0.18	0.75	0.58	0.39	0.36	-0.29	---												
Sc	0.72	0.17	0.87	0.40	-0.39	-0.02	0.13	0.47	-0.05	---											
Rb	-0.50	0.52	-0.48	0.27	0.60	0.12	0.01	-0.62	0.67	-0.48	---										
Br	0.88	-0.02	0.87	0.07	-0.56	-0.24	-0.12	0.37	-0.46	0.79	-0.59	---									
Zn	0.12	-0.16	0.20	0.00	-0.13	-0.06	-0.03	0.13	-0.09	0.27	-0.22	0.21	---								
Co	-0.21	-0.02	-0.22	-0.06	0.11	-0.09	-0.12	-0.25	0.01	-0.31	0.13	-0.23	0.52	---							
K	-0.40	0.69	-0.29	0.60	0.60	0.28	0.19	-0.49	0.87	-0.28	0.79	-0.49	-0.29	-0.03	---						
La	-0.32	0.81	-0.25	0.73	0.70	0.32	0.28	-0.47	0.91	-0.19	0.74	-0.47	-0.23	0.05	0.91	---					
Mn	-0.33	-0.54	-0.36	-0.62	-0.04	-0.36	-0.39	-0.27	-0.46	-0.46	-0.08	-0.23	0.02	0.36	-0.34	-0.38	---				
Ti	-0.63	0.40	-0.54	0.23	0.73	0.07	-0.05	-0.67	0.68	-0.53	0.83	-0.74	-0.33	0.04	0.76	0.75	-0.03	---			
V	-0.43	0.59	-0.36	0.59	0.46	0.53	0.39	-0.33	0.85	-0.26	0.68	-0.55	-0.33	-0.07	0.85	0.85	-0.33	0.76	---		
Al	-0.35	0.63	-0.25	0.58	0.54	0.29	0.15	-0.53	0.78	-0.18	0.64	-0.45	-0.30	-0.04	0.78	0.84	-0.31	0.77	0.92	---	
Na	-0.38	0.18	-0.37	-0.02	0.39	-0.19	-0.29	-0.55	0.21	-0.45	0.36	-0.46	0.12	0.51	0.34	0.34	0.28	0.40	0.17	0.23	---
Element	Sm	Ce	U	Th	Hf	As	Sb	Fe	Cr	Sc	Rb	Br	Zn	Co	K	La	Mn	Ti	V	Al	Na

Note: shading indicates statistically significant correlation at 95 % confidence and $p < 0.0001$.

Table 8. Correlation matrix of elemental data, excluding Bog Iron samples.

Element																					
Sm	---																				
Ce	0.34	---																			
U	0.74	0.29	---																		
Th	0.13	0.80	0.31	---																	
Hf	-0.31	0.40	-0.30	0.37	---																
As	-0.46	0.42	-0.39	0.56	0.29	---															
Sb	-0.40	0.53	-0.31	0.70	-0.41	0.91	---														
Fe	-0.10	0.10	0.02	0.17	-0.22	0.31	0.34	---													
Cr	-0.26	0.69	-0.12	0.81	0.50	0.78	0.86	0.20	---												
Sc	0.75	0.50	0.88	0.49	-0.18	-0.22	-0.11	0.04	0.15	---											
Rb	-0.36	0.42	-0.36	0.37	-0.39	0.57	0.60	0.03	0.65	-0.20	---										
Br	0.87	0.13	0.87	0.06	-0.44	-0.56	-0.50	-0.10	-0.39	0.76	-0.45	---									
Zn	0.03	-0.13	0.08	-0.02	-0.03	-0.13	-0.13	-0.13	-0.04	0.08	-0.11	0.09	---								
Co	-0.14	-0.10	-0.15	-0.06	-0.01	-0.03	-0.02	-0.19	-0.07	-0.23	-0.02	-0.15	0.63	---							
K	-0.24	0.69	-0.10	0.77	0.42	0.77	0.83	0.27	0.89	0.12	0.67	-0.31	-0.19	-0.21	---						
La	-0.16	0.80	-0.07	0.87	0.58	0.73	0.85	0.11	0.93	0.17	0.61	-0.32	-0.14	-0.08	0.88	---					
Mn	-0.29	-0.65	-0.32	-0.63	-0.17	-0.38	-0.42	-0.37	-0.57	-0.47	-0.28	-0.16	0.07	0.33	-0.58	-0.57	---				
Ti	-0.56	0.30	-0.54	0.33	0.59	0.68	0.68	-0.03	0.64	-0.36	0.72	-0.71	-0.30	-0.16	-0.62	0.65	-0.22	---			
V	-0.33	0.54	-0.25	0.66	0.30	0.93	0.88	0.22	0.84	-0.03	0.59	-0.46	-0.28	-0.19	0.82	0.81	-0.46	0.73	---		
Al	-0.20	0.57	-0.12	0.70	0.34	0.81	0.77	0.09	0.76	0.11	0.44	-0.33	-0.28	-0.20	0.70	0.79	-0.50	0.65	0.93	---	
Na	-0.23	0.01	-0.24	-0.01	0.15	0.03	-0.01	-0.22	0.03	-0.25	0.02	-0.30	0.29	0.48	0.03	0.09	0.22	0.05	-0.07	-0.09	---
Element	Sm	Ce	U	Th	Hf	As	Sb	Fe	Cr	Sc	Rb	Br	Zn	Co	K	La	Mn	Ti	V	Al	Na

Note: shading indicates statistically significant correlation at 95 % confidence and $p < 0.0001$.

Table 9. Correlation matrix of elemental data, excluding Bog Iron and Om/Ah samples of the depression.

Element																					
Sm																					
Ce	0.42																				
U	0.44	0.80																			
Th	0.10	0.80	0.79																		
Hf	0.08	0.49	0.44	0.45																	
As	-0.09	0.58	0.45	0.73	0.07																
Sb	-0.05	0.67	0.53	0.85	0.26	0.88															
Fe	0.02	0.17	0.10	0.20	-0.25	0.35	0.37														
Cr	0.05	0.79	0.69	0.90	0.39	0.77	0.87	0.23													
Sc	0.37	0.80	0.84	0.84	0.30	0.58	0.70	0.30	0.86												
Rb	0.04	0.55	0.37	0.47	0.22	0.43	0.48	0.02	0.59	0.45											
Br	0.56	0.11	0.14	-0.13	0.04	-0.25	-0.26	-0.18	-0.19	-0.06	0.13										
Zn	-0.12	-0.15	-0.20	-0.04	0.03	-0.07	-0.07	-0.14	-0.01	-0.10	-0.05	-0.16									
Co	0.02	-0.07	-0.10	-0.04	-0.07	-0.13	-0.10	-0.24	-0.12	-0.18	-0.11	0.05	0.67								
K	-0.02	0.76	0.61	0.83	0.33	0.76	0.83	0.30	0.86	0.75	0.63	-0.13	-0.16	-0.26							
La	0.14	0.88	0.77	0.95	0.51	0.71	0.86	0.14	0.92	0.83	0.56	-0.09	-0.12	-0.12	0.87						
Mn	-0.29	-0.66	-0.54	-0.62	-0.27	-0.57	-0.58	-0.40	-0.69	-0.70	-0.42	0.01	0.10	0.31	-0.66	-0.67					
Ti	-0.05	0.50	0.42	0.53	0.41	0.53	0.56	-0.07	0.57	0.43	0.61	-0.24	-0.31	-0.36	0.60	0.63	-0.47				
V	0.00	0.64	0.55	0.77	0.12	0.93	0.87	0.26	0.81	0.67	0.48	-0.23	-0.25	-0.28	0.80	0.79	-0.60	0.65			
Al	-0.01	0.62	0.60	0.77	0.20	0.84	0.79	0.15	0.73	0.63	0.35	-0.23	-0.27	-0.24	0.68	0.77	-0.60	0.64	0.93		
Na	0.01	0.04	0.07	0.01	0.02	-0.16	-0.17	-0.26	-0.09	-0.04	-0.14	-0.07	0.34	0.46	-0.06	-0.01	0.18	-0.22	-0.23	-0.21	
Element	Sm	Ce	U	Th	Hf	As	Sb	Fe	Cr	Sc	Rb	Br	Zn	Co	K	La	Mn	Ti	V	Al	Na

Note: shading indicates statistically significant correlation at 95 % confidence and $p < 0.0001$.

4.4.4. Principal component analysis

Principal component analysis (PCA) was conducted on the complete NAA data set, then repeated without the Bog Iron and Om/Ah samples of the depression. PCA is a type of multivariate statistical analysis where no groupings of variables are assumed *a priori*, and no dependent or independent variables are assigned (Rencher, 1995). The result is a clustering of the variables according to similarities with one another, in this case, with respect to distribution and concentration. PCA was performed to evaluate the natural groupings of elements analyzed for this study, with the intent of providing insight into arsenic geochemistry in these soils.

Usually, elements that were significantly correlated (Section 4.4.3) were also part of the same cluster (Figures 8, 9, and 10), but not always. Correlation coefficients compare one element against only one other element at a time; whereas PCA simultaneously considers the entire data set and finds the most significant groupings. Therefore, some differences between the two approaches are to be expected. The average R^2 value for the complete data set (0.7434) is very close to that for the data excluding the Bog Iron samples (0.7406). The average R^2 without the Bog Iron or Om/Ah samples is 0.6976.

Arsenic and Sb are grouped together on Figures 8, 9, and 10. They are both elements of Group V on the Periodic Table and are, therefore, expected to have similar geochemical behaviour and occur together in soil. However, by the same principle, K and Rb should also be in the same grouping, but are not in one instance (Figure 8). Without the Bog Iron samples, many elements that are either a component of or are commonly associated with clays (*i.e.*, Al, K, Ti, V, Rb) are grouped together (Figure 9). As discussed earlier, the chemical conditions under which the Bog Iron and Om/Ah layers formed were different from the other soil horizons of the study. Excluding them from the cluster analysis allows trends occurring in the other horizons to become apparent (Figure 10).

Some of the elements of the fourth group on Figure 8 (Sm, U, Br, Sc, Co) are known to have an affinity for organic matter and, thus, often exhibit higher concentrations in organic matter-rich soils, such as the Om/Ah layer of the depression. Uranium, for example, is very soluble and occurs in the hexavalent oxidation state (U^{6+})

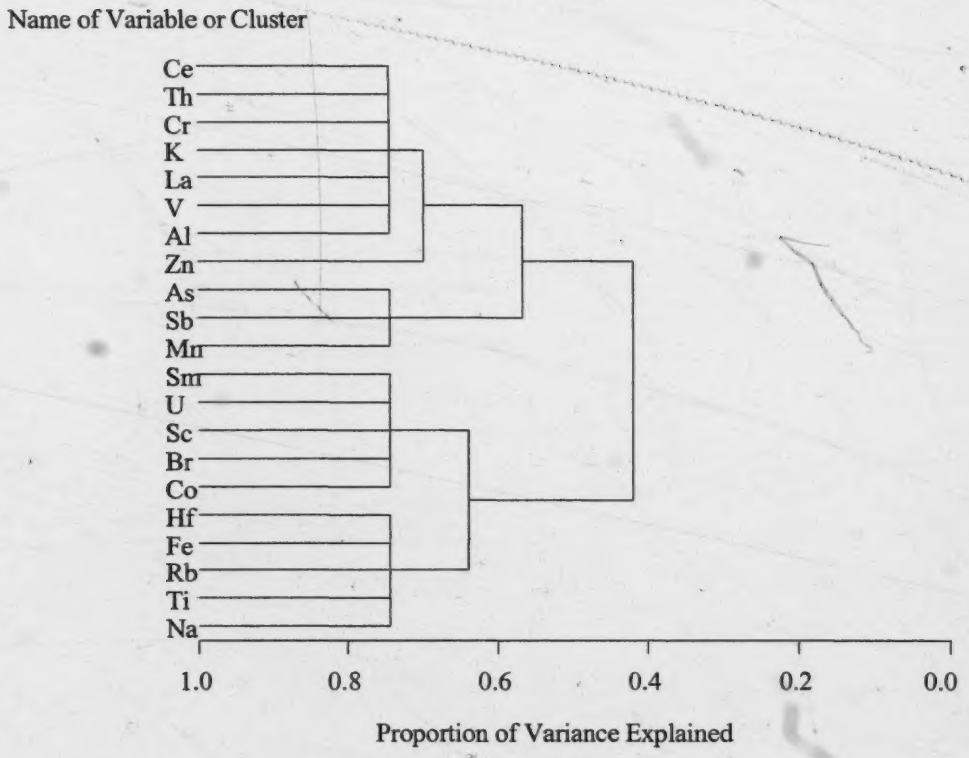

Figure 8. Dendogram for all samples.

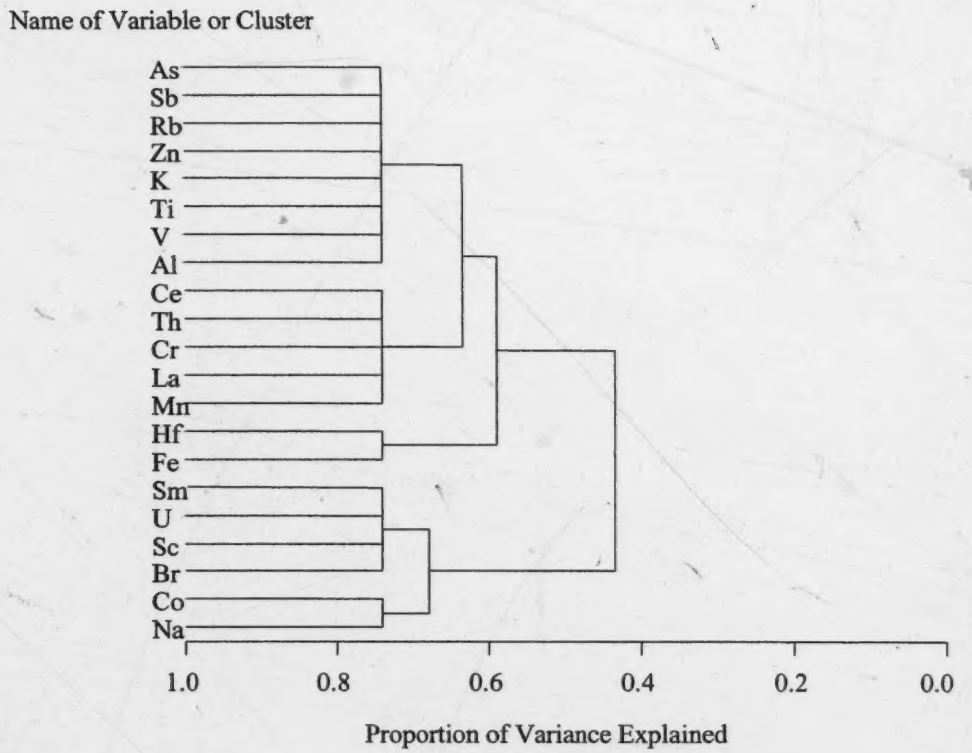

Figure 9. Dendogram excluding Bog Iron samples.

under oxidizing conditions. Under reducing condition, U is reduced to the quadravalent ion (U^{4+}) and can precipitate or be adsorbed from solution (Langmuir, 1978). Bromine is well known to accumulate in peat (Krauskopf, 1967). With the Bog Iron samples removed (Figure 9), four of the elements (Sm, U, Sc, Br) remain in one group. As can be seen from Table A-4, these four elements are enriched relative to the other soil horizons and positions, due to the physico-chemical conditions and accumulation of organic matter in the Om/Ah horizon. Once the Om/Ah data are excluded and the PCA repeated (Figure 10), the Sm, U, Sc, and Br grouping disappears.

PCA showed As to be grouped with elements commonly associated with clays. It was expected that As and Fe would be grouped together, due to arsenic's strong affinity for iron oxides (Section 2.2). However, they were not in the same group in any case (Figures 8, 9, or 10).

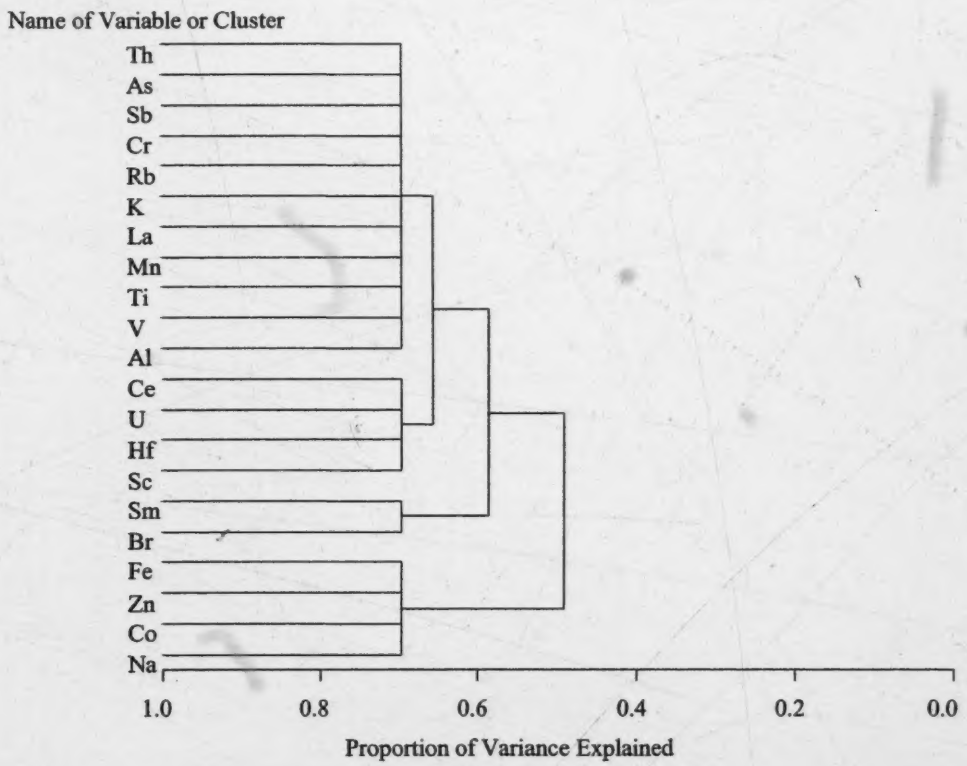

Figure 10. Dendogram excluding Bog Iron and Om/Ah samples of the depression.

4.4.5. Mineralogy

As discussed in Section 4.1, the main clay minerals observed in the Boundary Soils were kaolinite and micas. Potassium is a component of micas, which were found to be more prevalent in the lower solum of Boundary Soil, and can be used as an indication of amount of mica in soil. In previous studies, jarosite [$KFe_3(SO_4)_2(OH)_6$] was observed in greater amounts in the lower solum than the upper solum (Pawluk and Dudas, 1978; Bulmer, 1987; Dudas *et al.*, 1988), and yellow stones/mineral fragments, likely jarosite, were observed in some lower horizon samples (T3 Bfj2 M, T3 C M, T3 Cg T; Table A-3, Appendix) of the current study. The distribution of K in the soils studied (Figure 11) might reflect the distribution of micas and jarosite, with K concentrations generally greater in the B2 and C horizons relative to the A and B1 horizons.

Clays of marine origin often have high potassium concentrations. The average concentration of K in the soils studied was 21,000 $\mu g\ g^{-1}$ (all samples), higher than that reported in acid sulphate soils of marine origin in Thailand (12,000 to 17,000 $\mu g\ g^{-1}$; as reported in Bloomfield and Coulter, 1973).

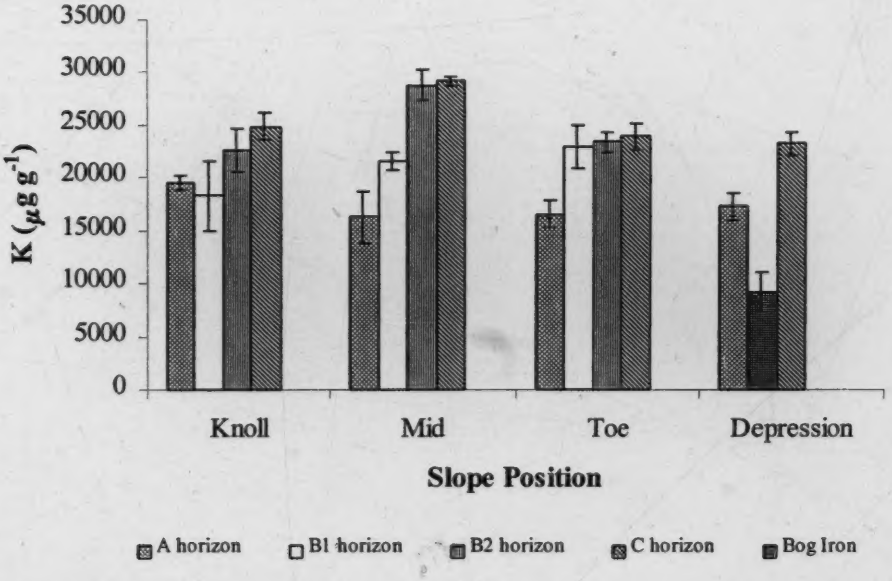

Figure 11. Average total potassium concentrations in soil horizons along the slope.

Aluminum is a major component of many minerals, including those identified as being dominant in the Boundary Soils (*e.g.*, kaolinite, micas). The distribution of Al in these soils (Figure 12) reflects the relatively low clay content (observed by manual texturing; Table A-3, Appendix) of the A horizon at all slope positions, and of the Bog Iron layer. The slightly higher Al concentrations in the B2 horizon samples agrees with Bulmer's (1987) particle size analyses of these soils, which showed greatest clay content in the lower B and BC horizons.

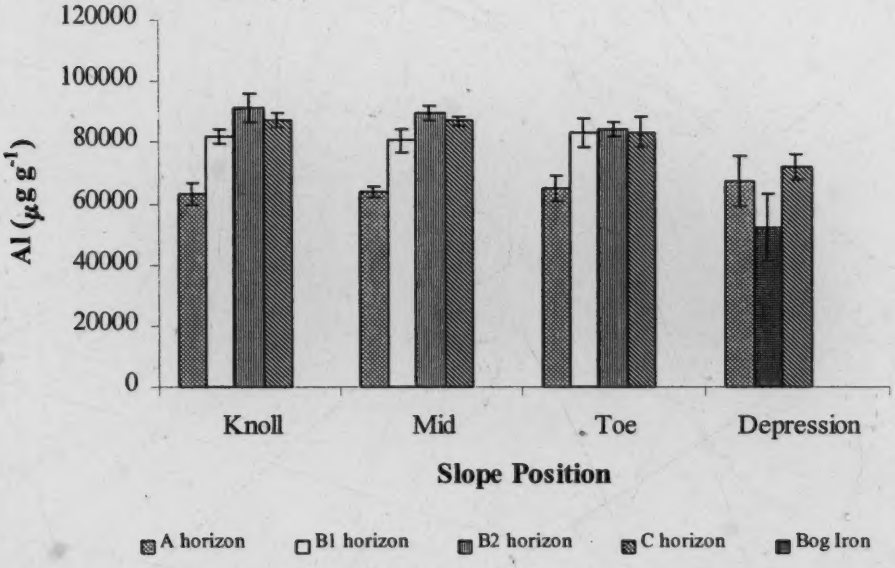

Figure 12. Average total aluminum concentrations in soil horizons along the slope.

Sodium in these soils is likely primarily contained in natrojarosite. Higher Na in the C horizons at knoll and mid-slope positions (Figure 13) may be a reflection of natrojarosites in the lower profile at upper slope positions that were observed by Bulmer (1987) and Dudas *et al.* (1988; Table A-2, Appendix). Feldspar content and/or distribution has not been studied in these soils, therefore distribution of Na in these soils as a reflection of feldspars is unknown. The reason for the elevated Na in the A horizon at knoll top may be a result of evaporative accumulation of salts, as the knoll top is likely well-drained the majority of the time.

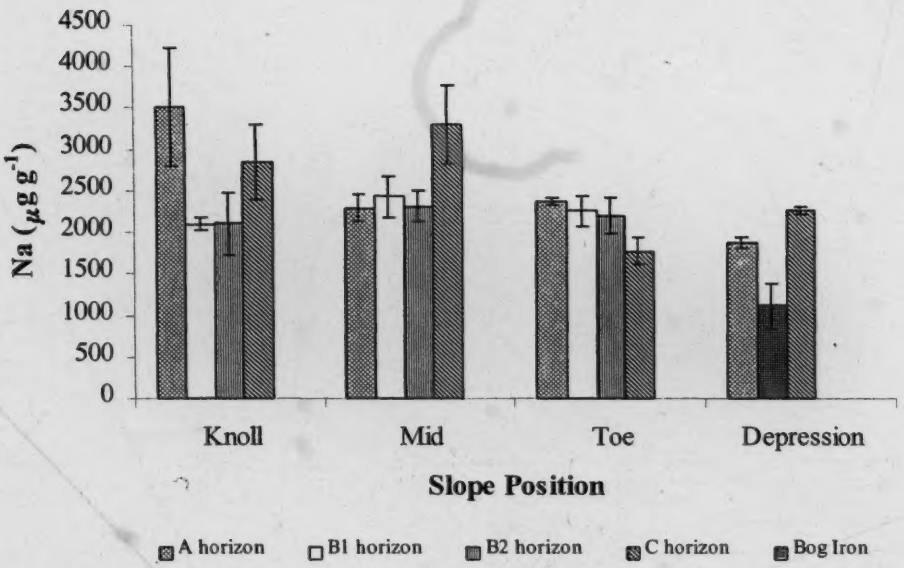

Figure 13. Average total sodium concentrations in soil horizons along the slope.

Iron minerals are an abundant and important component of acid sulphate soils. They are discussed separately in Section 4.6.

4.5. GROUNDWATER ANALYSIS

Three groundwater samples (T1, T2, and T3) were collected for this study, one from each of the three soil sampling pits in the depression at the bottom of the slope (Figure 3). Eh, EC, pH, and concentrations of ten dissolved cations were measured on each sample (Table 10).

Calcium is higher in groundwater from the study site (average 346 mg L^{-1}) than average Alberta groundwater (63 mg L^{-1}; Fitzgerald *et al.*, 1997) and Thai acid sulphate soil solution (average 154 mg L^{-1}; van Breemen and Harmsen, 1975). Calcium is more soluble at low pH (Clark, 1966), hence the higher concentrations in acidic soils. The reason for more Ca in Boundary acid sulphate soils than in Thai acid sulphate soils may be greater abundance of gypsum ($CaSO_4 \bullet 2H_2O$). Large gypsum crystals were observed throughout a sample of Boundary Soil parent material, approximately 10 m below ground surface.

Table 10. Redox potential, electrical conductivity, pH, and dissolved cations in groundwater.

Sample	Ca	Na	Al	Mg	K	Fe	Mn	Se	As	Mo	Eh	EC	pH
					$mg\ L^{-1}$						mV	$dS\ m^{-1}$	
T1	346	54.6	41.6	35.6	3.90	0.78	0.948	3.7E-03	4.0E-04	4.1E-05	613	1.69	3.96
T2	352	57.7	36.7	33.1	3.75	2.6	0.828	3.4E-03	3.7E-04	6.5E-05	611	1.95	3.93
T3	339	58.4	37.7	34.5	4.58	1.4	0.794	3.3E-03	4.1E-04	5.2E-05	598	2.19	3.97

Sodium was considerably lower in groundwater from the study site (average 56.9 mg L^{-1}) than average Alberta groundwater (325 mg L^{-1}; Fitzgerald *et al.*, 1997) and Thai acid sulphate soil solution (average 294 mg L^{-1}; van Breemen and Harmsen, 1975). This agrees with the lack of natrojarosite (relative to jarosite) observed in the Boundary Soils, and the low Na concentrations in soil in the depression (Figure 13).

Aluminum concentrations in the groundwater at the site (average 38.7 mg L^{-1}) are elevated relative to average groundwater in Alberta (0.15 mg L^{-1}; Fitzgerald *et al.*, 1997). The average falls within the range reported by van Breemen (1973; 0.62 to 57 mg L^{-1}) in groundwater from an area with oxidized pyritic mud in Thailand. High Al is expected in groundwater in the Boundary area, due to the acidic conditions causing dissolution of clays and other Al-containing minerals. Indeed, Al is usually the dominant exchangeable cation in very acid soils (pH 1.8 to 4; Bloomfield and Coulter, 1973).

Magnesium was slightly higher in groundwater at the site (average 34.4 mg L^{-1}) than average Alberta groundwater (25 mg L^{-1}; Fitzgerald *et al.*, 1997), but lower than young Thai acid sulphate soils (average 140 mg L^{-1}; van Breemen and Harmsen, 1975).

Potassium concentrations in groundwater at the site (average 4.1 mg L^{-1}) are average for Alberta groundwater (4.1 mg L^{-1}; Fitzgerald *et al.*, 1997), but low relative to groundwater associated with young acid sulphate soils in Thailand (average 23.9 mg L^{-1}; van Breemen and Harmsen, 1975). One possible explanation is that K-containing minerals, such as mica and orthoclase feldspar, may be more abundant in the Thai parent material and soils.

The average Fe concentration in groundwater at the site (1.59 mg L^{-1}) exceeds that of average Alberta groundwater (0.84 mg L^{-1}; Fitzgerald *et al.*, 1997). Higher than average Fe concentrations in groundwater at the study site are expected due to the pyritic parent material, the high levels of Fe in the soils, and the acidic conditions, which cause an increase in Fe solubility. Van Breemen and Harmsen (1975) report higher dissolved Fe concentrations (112 to 782 mg L^{-1}) in areas of Thailand with young acid sulphate soils.

Manganese was higher in the groundwater from the study site (average 0.857 mg L^{-1}) than the average Alberta groundwater (0.135 mg L^{-1}; Fitzgerald *et al.*, 1997), likely because of its increased solubility at low pH. Manganese in groundwater was lower than that of young acid sulphate soils in Thailand (average 6.04 mg L^{-1}; van Breemen and Harmsen, 1975).

Selenium levels in the groundwater at the site (average 0.0035 mg L^{-1}) were comparable to those in average Alberta groundwater (0.002 mg L^{-1}; Fitzgerald *et al.*, 1997).

The concentration of As in groundwater samples from the Boundary Soils area (average 0.00039 mg L^{-1}) was less that of average Alberta groundwater (0.004 mg L^{-1}; Fitzgerald *et al.*, 1997). Both of these averages are below the Guideline for Canadian Drinking Water Quality (0.025 mg L^{-1}; CCME, 1999). Section 4.7 includes a more extensive discussion on As in Boundary Soils and associated groundwater.

The average Mo concentration in groundwater samples (0.000053 mg L^{-1}) was lower than that of average Alberta groundwater (0.004 mg L^{-1}; Fitzgerald *et al.*, 1997). Molybdenum was measured in these groundwater samples, as it is known to be strongly associated with iron sulphide minerals (Morse *et al.*, 1987).

Average redox potential (Eh) and pH measured in the groundwater samples (607 mV and 3.95, respectively) agree well with soil Eh and pH [average 510 mV and 4.23 (saturated paste), respectively]. The pH of Thai acid sulphate soil solution is comparable (4.11; van Breemen and Harmsen, 1975). Acidity resulting from pyrite oxidation maintains redox potential at high voltage. Clark (1966) reported Eh of 600 to 800 mV and pH of 1.5 to 3.8 in water in the vicinity of oxidizing pyrite. Van Breemen (1973)

reported pH values from 2.8 to 5.5 in groundwater in a pyrite oxidizing area. pH tends to be lower (and, hence, Eh is higher) during the active oxidizing stages.

Average EC in groundwater at the site (1.94 dS m^{-1}) was similar to that of average Alberta groundwater (1.65 dS m^{-1}; Fitzgerald *et al.*, 1997), but lower than that of groundwater of the Kaskapau Formation, reported as 2,000 to 4,000 mg L^{-1} total dissolved solids (equivalent to approximately 3 to 6 dS m^{-1}; Ozoray, 1982; Section 2.6.2). However, higher conductivity would be expected of deeper rather than more shallow groundwater, as deeper water generally accumulates more dissolved solids from traveling for a longer period of time through relatively salt-rich materials.

EC is often much higher in acidic rather than neutral water, as the acid conditions cause solubilization of many constituents, thus contributing dissolved solids to water. Bloomfield and Coulter (1973) describe considerable salt accumulations (EC up to 10 dS m^{-1}) known to occur upon drying of oxidized, pyritic soils. Clark (1966) reports an ionic strength of 0.3 mol L^{-1} (approximately 23 dS m^{-1}) as typical of mine water. EC of shallow groundwater at the site may have been higher during the active stages of pyrite oxidation.

Although anions were not measured as part of this study, SO_4^{2-} concentrations were estimated by assuming that SO_4^{2-} is the dominant anion in groundwater of the area. Ozoray (1982) reports SO_4^{2-} as the dominant anion in groundwater of the Kaskapau Formation, constituting greater than 60 % of total anion milliequivalents (meq; Section 2.6.2). The cations measured in the groundwater samples collected contribute approximately 27 meq L^{-1}, therefore, SO_4^{2-} should contribute between 60 and 100 % of anion equivalents (16 to 27 meq L^{-1}). This range translates to approximately 770 to 1,300 mg L^{-1} SO_4^{2-}. According to the literature, these concentrations are slightly lower than expected in water in the vicinity of acid sulphate soils. Bloomfield (1972) reports 1,450 mg SO_4^{2-} L^{-1} in a drainage ditch of a reclaimed coal mine site. Van Breemen (1973) measured SO_4^{2-}concentrations of 1,500 to 25,000 mg L^{-1} in leachates of oxidizing pyritic mud in Thailand. Elevated SO_4^{2-} concentrations would be expected in actively oxidizing pyritic material, and in waters associated with them. The Boundary Soils are post-active and, therefore, might reasonably be expected to have lower concentrations of

soluble constituents such as SO_4^{2-}. Average Alberta groundwater contains 283 mg SO_4^{2-} L^{-1} (Fitzgerald *et al.*, 1997).

In summary, Ca and Na are the dominant cations in groundwater at the study site; arsenic is present in very low quantities (0.00039 mg L^{-1}). Sulphate is the dominant anion in groundwater at the site, with a calculated concentration range of 770 to 1,300 mg L^{-1}.

4.6. IRON

4.6.1. Distribution in Boundary Soil Catena

Distribution of total iron in soil along the slope is shown in Figure 14. In most samples, Fe concentrations were at levels typical of soil derived from shale parent material (approximately 47,000 μg g^{-1}; Taylor and McLellan, 1985), with an average of 48,700 μg g^{-1} (excluding the Bog Iron samples). Concentrations in the Bog Iron layer in the depression, however, were considerably higher: 414,000 μg g^{-1} (T1), 137,000 μg g^{-1} (T2), and 329,000 μg g^{-1} (T3). The average concentration of Fe in the Bog Iron layer (293,000 μg g^{-1}) is higher than many reported concentrations of pyrite in acid sulphate soils (32,000, 60,000, and 68,000 μg g^{-1}; Bloomfield, 1972) and in mine tailings (100,000 to 250,000 μg g^{-1}; Al *et al.*, 1994), and pyrite has two moles of S for every mole of Fe. The average Fe concentration in the Bog Iron layer is higher than that of most Bf horizons of Podzolic soils found in Canada (*e.g.*, 19,000 μg g^{-1} dithionite citrate bicarbonate-extractable iron; Courchesne and Hendershot, 1989), and slightly higher than acid-extractable iron oxides reported for a Xanthic Ferralsol from Brazil (approximately 250,000 μg g^{-1} Fe_2O_3; Wambeke, 1974).

When plotted on the same graph, the high levels of iron in the Bog Iron layer mask variations in the other locations. Therefore, Fe was also plotted excluding the Bog Iron layer (Figure 15). Iron generally increases in concentration down slope, and is greatest at the toe and in the depression, suggesting Fe may have been solubilized, translocated down slope in solution, and accumulated at the base of the slope.

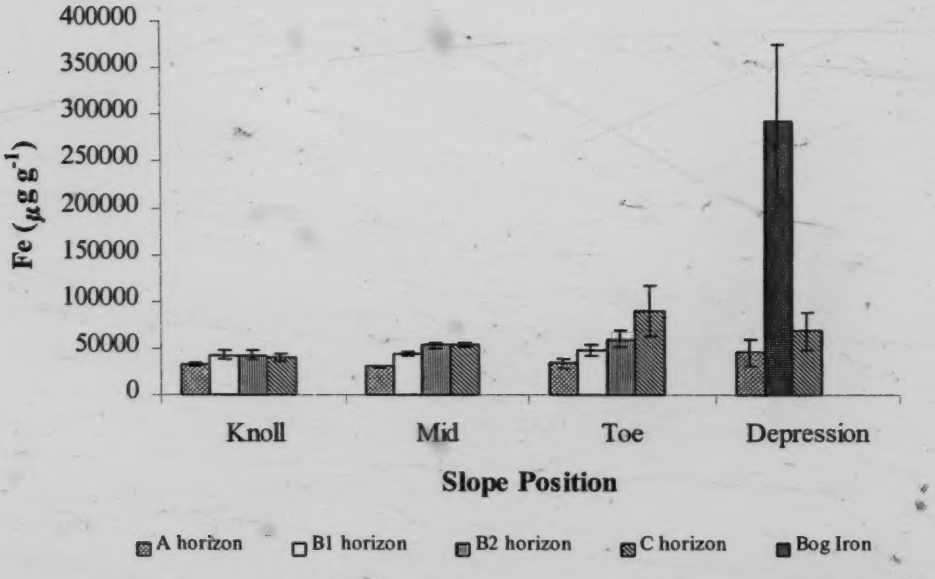

Figure 14. Average total iron concentrations in soil horizons along the slope.

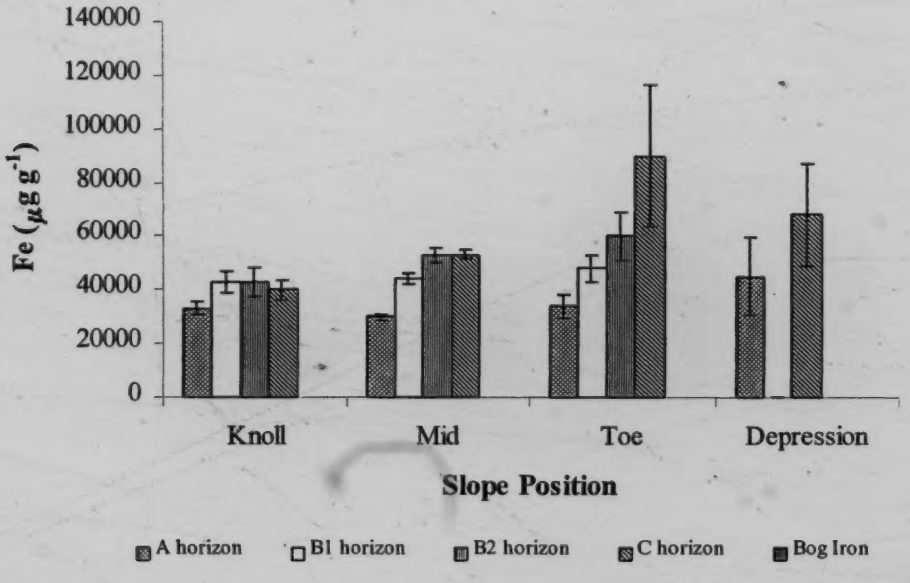

Figure 15. Average total iron concentrations (excluding Bog Iron samples) along the slope.

Organic matter in the A horizons at the knoll, mid, and toe positions may be diluting iron concentrations. Despite the high organic matter content of the Om/Ah horizon in the depression, the average Fe concentration in this layer is high relative to the surface horizons at other slope positions. Thus, Fe appears to have been translocated down slope and is, in effect, depleted in upper slope positions.

Other evidence supportive of the down-slope translocation of Fe is the change in colour of the B horizon from the toe of the slope to the depression. Goethite is generally in the 7.5YR and 2.5Y range; hematite is typically 5YR and redder (Schwertmann and Taylor, 1989). The Munsell colour of the B horizon at the toe was yellowish brown (10 YR 5/4 to 3/4 to 3/6) to dark yellowish brown (10 YR 4/6), and that of the Bog Iron layer was variations of red and reddish brown (all descriptions were in the 5YR and 2.5YR range; Table A-3). These colours suggest a change in the type of iron oxides present from the toe of the slope to the depression.

The prevailing acidic conditions that have historically occurred in these soils would have promoted iron solubility (ferrous iron is dominant at low pH; Figure 17). EC and pH data are consistent with down slope translocation of soluble constituents, with EC increasing and pH decreasing down slope (Figure 7 and Figure 5, respectively).

4.6.2. Characterization of Bog Iron Layer

The highly concentrated Fe layer in the depression (Figure 3) was a 10 cm-thick, bright red layer with abundant organic matter, roots, and decomposed and semi-decomposed leaves and wood (Table A-3, Appendix). The term "Bog Iron" was given to this layer on account of its distinct features.

At the time of sampling, this horizon was saturated, but oxidized, as evidenced by the bright red colour of the Fe. Redox measurements and Munsell colour observations are consistent with this observation. Under reducing conditions, the Fe would display the grayish-green colour characteristic of ferrous iron.

This Fe layer is not considered a ferric (Bf) horizon, the characteristic horizon of the Podzolic order of the Canadian System of Soil Classification (Agriculture Canada, 1987). Bf horizons are formed by podzolization, when Fe and Al are leached from the surface horizon into the B horizon, where they are immobilized by organic compounds. The leaching process is usually driven by the generation of organic acids from the

decomposition of plant material on the soil surface (Buol *et al.*, 1997). The Bog Iron layer does not comply with the above definition, as the acidity in the Boundary Soils arises from pyrite oxidation, not plant decomposition, and Al is not accumulating in the Bog Iron layer along with the Fe [lowest average Al concentration (52,000 $\mu g\ g^{-1}$) occurs in the Bog Iron layer].

X-ray diffraction analysis revealed that hematite (α-Fe_2O_3) is the dominant iron oxide in the Bog Iron layer, indicated by the large peaks at 39 and 42 degrees 2θ (Figure 16). Diffractograms for the Bog Iron deposit from Transects 2 and 3 also show that hematite is the most prevalent mineral (Figures AI-1 and AI-2, Appendix). Munsell colours of the Bog Iron layer, in the 5YR to 2.5YR range (Table A-3, Appendix), are typical of hematite (Schwertmann and Taylor, 1989).

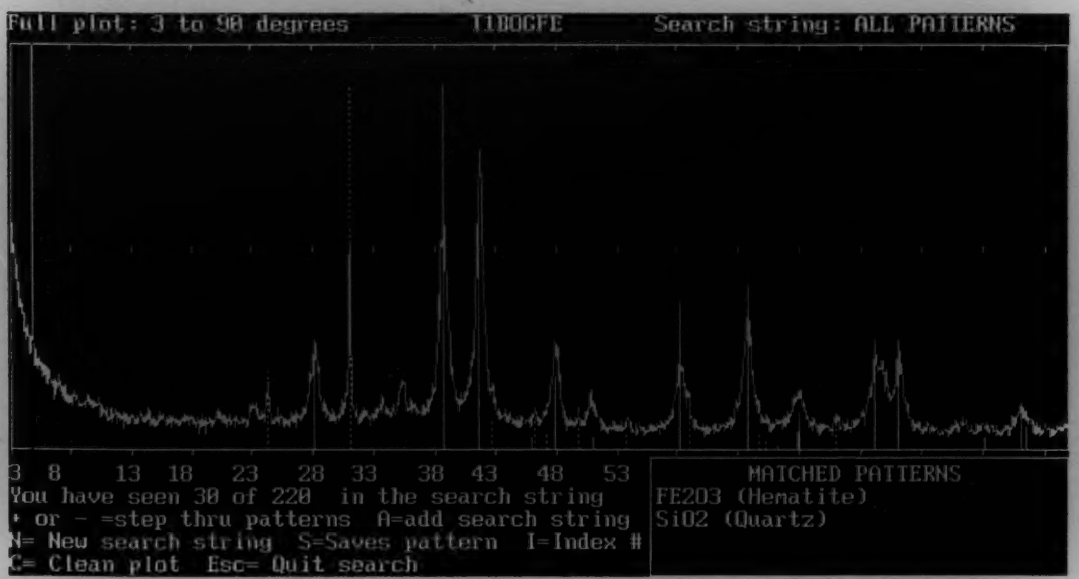
Full plot: 3 to 90 degrees
T1B0CFE
Search string: ALL PATTERNS
3 8 13 18 23 28 33 38 43 48 53
You have seen 30 of 220 in the search string
+ or - =step thru patterns A=add search string
N= New search string S=Saves pattern I=Index #
C= Clean plot Esc= Quit search
MATCHED PATTERNS
FE2O3 (Hematite)
SiO2 (Quartz)

Figure 16. X-ray diffraction patterns for Bog Iron soil from Transect 1.
(Solid vertical lines illustrate position of diffraction for hematite; dotted lines show position for quartz.)

Hematite is generally present in well-drained, seldomly reduced, highly weathered soils and is known for its red colour (Lindsay, 1979; Allen and Hajek, 1989). It is a product of advanced soil weathering. Quartz was present as a minor component of the Bog Iron layer in Transect 1. The diffractogram from Transect 2 (Figure A-1,

Appendix) shows that silicate minerals (quartz and clay) comprise a more significant component of the minerals than the Transect 1 sample. XRD analysis of Transect 3 Bog Iron deposit (Figure A-2) indicated that, in addition to hematite, maghemite (γ-Fe_2O_3) is present, and quartz makes up a significant proportion of minerals in the sample.

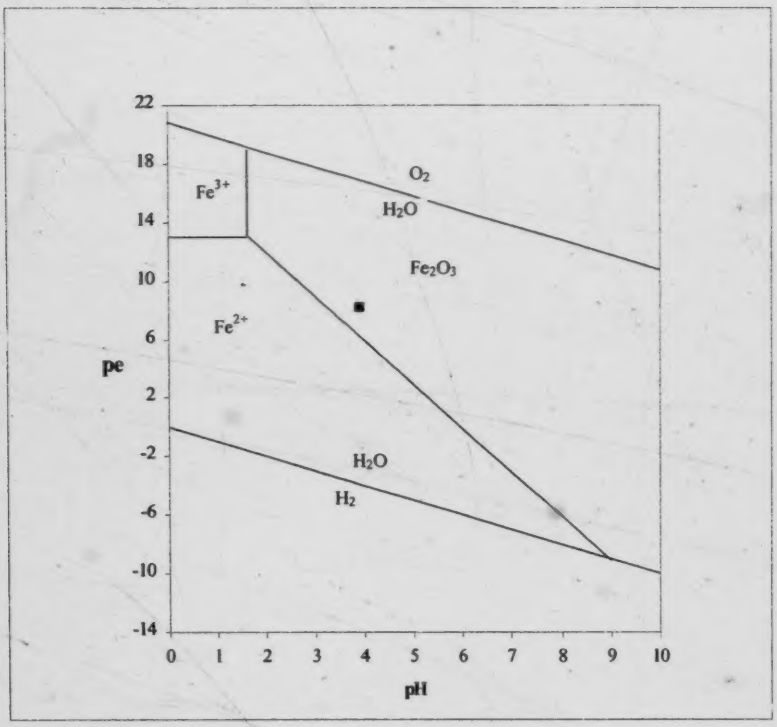

Figure 17. *pe*-pH diagram for Fe-O system.

Figure 17 shows the thermodynamically stable realm under which water and various Fe species exist. Redox potential is often expressed as *pe*, which has compatible units with pH. *pe* is the negative log of the electron activity, and is obtained *via* the Nernst equation:

$$pe = \frac{F}{2.303RT}(Eh)$$

which, when the Faraday constant (F; 23.062 kcal $volt^{-1}$ $equivalent^{-1}$), gas constant (R; 1.987 cal deg^{-1} mol^{-1}) and temperature (T; standard = 298 K) are substituted, becomes:

$$pe = \frac{Eh\ (mV)}{59.2}$$

(Lindsay, 1979).

The square on Figure 17 represents the average pH (3.92 in saturated paste extract) and the average Eh (483 mV; *pe* = 8.16) for the soil samples from the Bog Iron layer in the depressional area. Thus, in an Fe-O system, soil conditions of this study favour iron in the form of hematite (Fe_2O_3), which is consistent with XRD results.

Bulmer (1987) and Dudas *et al.* (1988) found that goethite then hematite were the dominant iron oxides in the B horizon of Boundary Soils. Evidence for goethite did not appear in the Bog Iron diffractograms.

4.6.3. Plant Opal

A one centimetre-thick layer of plant opal was present within the Bog Iron layer of Transect 1. "Plant opal" is a term applied to silicious microfossils that are generated when silica accumulates in plant tissues and persists after the living parts have decayed. Plant opal is also called "biogenic opal", "opal phytoliths", and/or "silica bodies", and is composed of hydrated, amorphous silica ($SiO_2 \bullet nH_2O$; Rovner, 1971).

The extremely low pH arising from acid sulphate soil genesis (Section 2.6.5) causes dissolution of many soil constituents, including silica minerals, such as clays and feldspars. Silica is also released during weathering of smectite to kaolinite, which often occurs during acid sulphate soil genesis. A silica-rich solution often results, and plant opal may form from silica precipitation. Plant opal was identified in acid sulphate soils of Thailand and the Netherlands (Buurman *et al.*, 1973).

Monosilic acid, a soluble form of silica, is taken up by plant roots, along with many other dissolved nutrients in water. While the other nutrients are utilized by the plant, the silica remains in the water and is transported throughout the plant until the water exits the plant *via* transpiration. The silica then precipitates out of solution and accumulates in the plant, often in the leaves, which are the site of transpiration (Rovner,

1971). Some primitive aquatic animals, such as sponges and diatoms, secrete silica as a component of their skeletons. These durable, siliceous shells often accumulate in soils as fossils after the organisms have died (Wilding and Drees, 1971).

Opal phytoliths range in size from 2 to 1000 μm, with most in the 20 to 200 μm range (Rovner, 1971). The specific gravity of opal phytoliths range from 1.5 to 2.3; they are generally colourless or light brown, but can be opaque. Darker colours are attributed to organic carbon occurring within the opal (Wilding and Drees, 1971). Plant opal of many different shapes can form, depending on the shape of the cell in which the silica was deposited (Blackman, 1971). The range of shapes include rods and dumbbells to trapezoids and discs (Baker, 1960; Rovner, 1971).

Plant opal has been used as a means of identifying the vegetational history of an area, which may reveal clues about soil and climatic history (Blackman, 1971; Rovner, 1971). However, there are limitations to using plant opal morphology for information, most notably that very diverse species of plants can contain plant opal of similar morphology (Blackman, 1971). Often, only general inferences can be made on broad changes in vegetation (Rovner, 1971).

The main limitation with attempting to identify the morphology of plant opal in the present study was the dearth of information on plant opal from Alberta, especially from the boreal forest. Many studies are from the northeastern United States and discuss trees such as beech, maple, and oak, none of which are native to Alberta. One study of plant opal in Alberta (Blackman, 1971) is of range grasses from the southern part of the province. Grass species were not observed at the study site, and range grasses would historically not have occurred in the area.

Scanning electron micrographs of some of the phytoliths present within the Bog Iron layer are shown in Plates 3 through 8. Energy-dispersive x-ray analysis was conducted on select specimens in the samples to determine the major elemental content and, thus, provided a measure of confidence in stating whether specimens were opal by evaluating their silicon content. Opal of many different shapes and sizes was present, from rod-shaped (Plate 3) and canoe-shaped (Plate 4) to spherical (Plate 5) and disc-like (Plate 6). Some had crenulated edges (Plate 7); others were perforated (Plate 8). Many fragments of specimens such as that in Plate 8 were present in the sample.

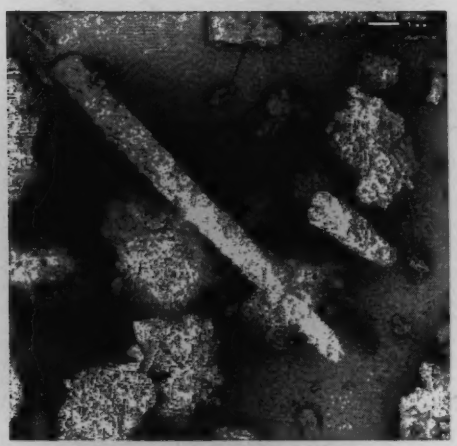

Plate 3. Rod-shaped plant opal
(scale bar is 10 μm).

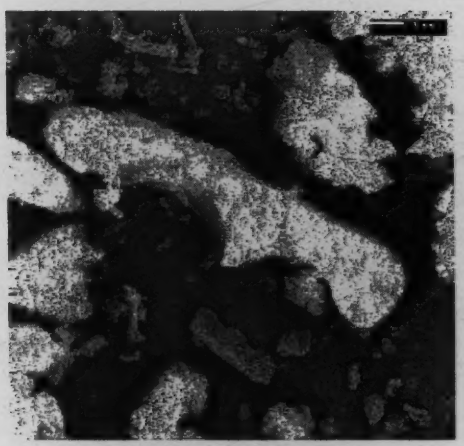

Plate 4. Canoe-shaped plant opal
(scale bar is 10 μm).

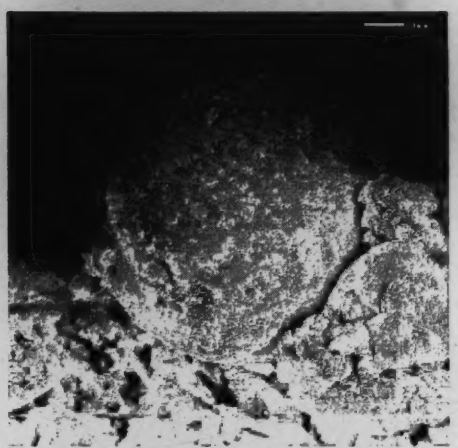

Plate 5. Spherical plant opal.
(scale bar is 1 μm).

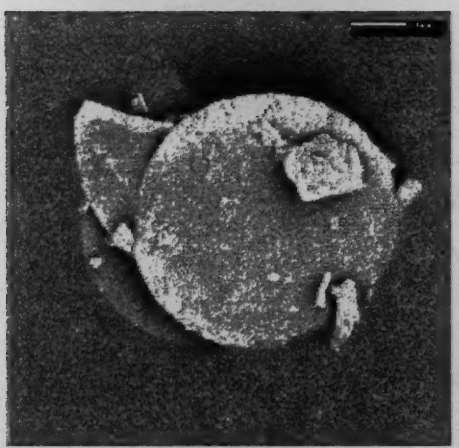

Plate 6. Disc-shaped plant opal.
(scale bar is 1 μm).

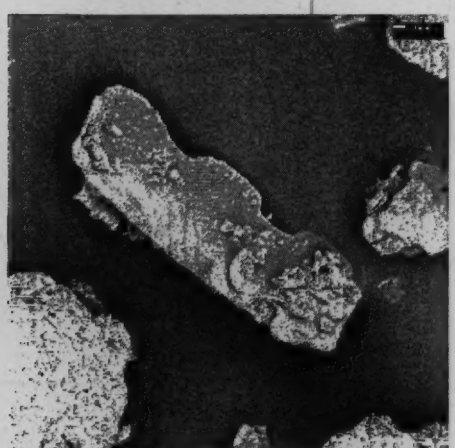

Plate 7. Plant opal with crenulated edges
(scale bar is 1 μm).

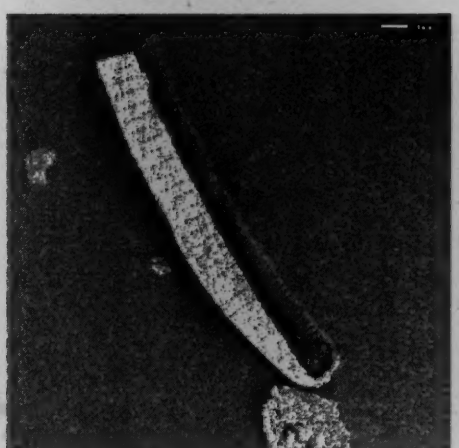

Plate 8. Perforated opal
(scale bar is 1 μm).

Plant opal micrographs from the current study were compared with those from the literature with the intent to gain information about the vegetational history of the site, and perhaps the formation of the Bog Iron layer. However, none of the phytoliths could be positively identified as arising from a specific type of plant or tissue. Discs (Plate 6) and globules have been associated with many different plants, for example white pine (*Pinus strobus*), foxtail (*Setaria lutescens*), and witch grass (*Panicum capillare*; Rovner, 1971). Rod-shaped opal (Plate 3) is present in nearly all plants, but is particularly abundant in Poacoid grasses, such as brome grass (*Bromus inermis*) and timothy (*Phleum pratense*). Blackman (1971) identified bluejoint (*Calamagrostis canadensis*) opal that resembles the specimen in Plate 7. Baker (1960) showed sketches of opal identical to that in Plate 7, but does not identify it, except to state that it is from diatomaceous earth of Holocene age from Western Victoria, Australia. The above-mentioned grasses (foxtail, brome, and timothy) are widespread species in Alberta and may have occurred on the study site in the past. Both timothy and brome are known to be acid-tolerant (lower pH limits of 4.5 and 5.0, respectively). However, timothy has high nutrient requirements and would likely not persist on the nutrient-depleted Boundary Soils (Hardy BBT Limited, 1989).

Jendrzejewski (1974) investigated fossils of numerous organisms with siliceous skeletons, which resembled the specimen in Plate 8. This specimen is likely a diatom. Fragments of these were observed throughout the sample, indicating an aqueous environment existed in the area at one point in time, as diatoms live in fresh water and marine habitats (Campbell, 1990).

Plant opal has been identified in other acid sulphate soils (Buurman *et al.*, 1973; van Breemen, 1982; van Breemen and Buurman, 1998). Although the solubility of silica decreases with decreasing pH (Mason and Moore, 1966), enough silica is in solution in acid sulphate soils to form plant opal. However, the relatively thick and pure deposit of plant opal observed in the aggregates of the Bog Iron soil is unusual compared to reports from other soils.

4.6.4. Geochemistry of Bog Iron Layer

As mentioned in Section 4.4, many elements in the Bog Iron layer exhibited unusual concentrations (either much higher or much lower) relative to the other horizons

on the site. The Bog Iron layer is approximately 40 % hematite; iron is so highly concentrated in this layer that many other elements are relatively depleted.

In the surficial environment, Al is one of the least soluble elements (Horowitz, 1991). As described by Astrom (1998), although Al is present in relatively high concentrations in the groundwater at the site (Section 4.5), the amount of Al in water is a small proportion (0.05 %) of that in the soil. Normalizing Fe, or any other element, to Al should give an indication of the loss or gain of the element relative to the relatively stable Al. Normalizing to Al also avoids differences in elemental concentrations between horizons due to variation in bulk density. Thus, normalizing to Al permits better assessment of translocation of elements within soil horizons and between slope positions. Figure 18 shows Fe normalized to Al. The Bog Iron layer has been omitted from Figure 18, as its Fe:Al ratio is 6.7 and minimizes the other columns on the figure.

Aluminum concentrations are lowest in the A horizons and relatively constant in the B1, B2, and C horizons along the slope (Figure 12). Therefore, the increasing ratios

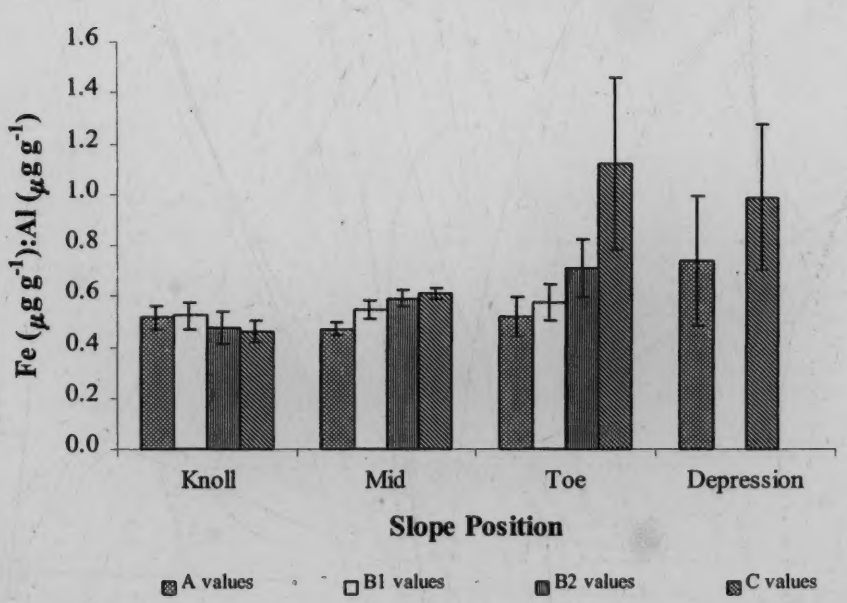

Figure 18. Iron to aluminum ratio in soil horizons along the slope.

down slope indicate that Fe is more concentrated than Al in the lower slope positions. Fe is more soluble than Al and was likely transported in solution down slope, where it precipitated and accumulated in the depression. Figure 18 verifies the observation of Fe enrichment in lower slope positions shown in Figure 14 and Figure 15.

The high concentration of Fe in the Bog Iron layer is also illustrated by graphing ratios of Fe to elements whose highest concentrations are in the Bog Iron layer. Of the 21 elements, only As, Sb, and Fe display their highest concentration in the Bog Iron layer. The large ratios in the Bog Iron layer are from proportionally much higher Fe in that layer than either As or Sb (Figure 19 and Figure 20). Again, Fe is elevated in all lower slope horizons relative to As and Sb. The two graphs of Fe:As and Fe:Sb are nearly identical, as As and Sb are both Group V elements and exhibit similar chemical behaviour.

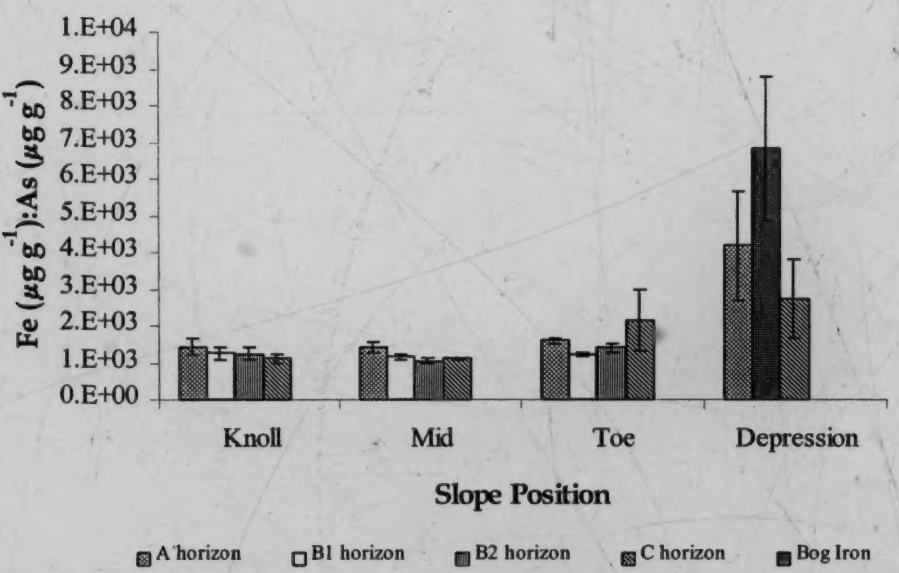

Figure 19. Iron to arsenic ratio in soil horizons along the slope.

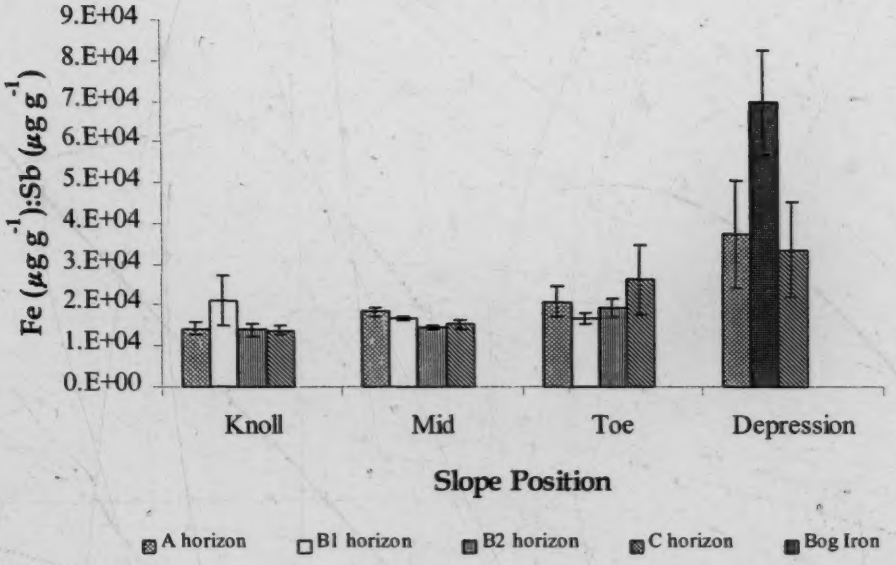

Figure 20. Iron to antimony ratio in soil horizons along the slope.

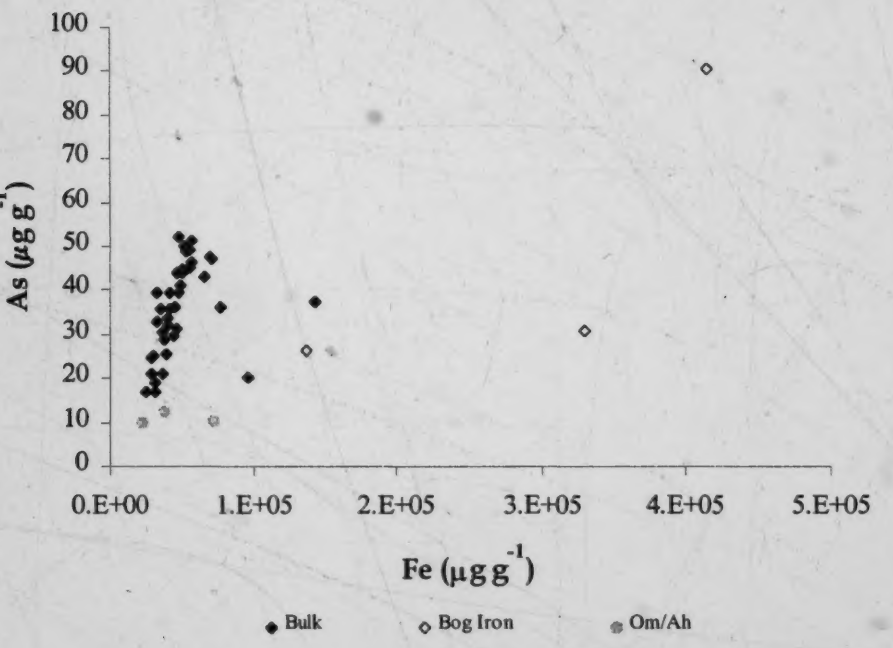

Figure 21. Iron versus arsenic, for all samples collected at the site.

Antimony and Fe are significantly correlated [correlation coefficient (r) = 0.62; Table 7]. Arsenic and Fe are positively correlated (r = 0.48; Figure 21), but not significantly (Tables 7, 8, and 9), likely due to the unusual chemistry of the Bog Iron layer. The samples from the Bog Iron layer (open triangles on Figure 21) deviate from the trendline of the other samples. Arsenic has been shown to adsorb more effectively to amorphous forms of iron (Pierce and Moore, 1982); it tends to not sorb as effectively to crystalline iron, such as that found in the Bog Iron layer (mainly hematite, Section 4.6.2).

4.6.5. Genesis of Bog Iron Layer

The general increasing concentrations of Fe down slope, increasing EC, decreasing pH, and the depth to shallow groundwater observed (approximately 40 cm, or bottom of B1 horizons) during sample collection are all indications that Fe is/was soluble and translocated down slope in water and accumulated at the base of the slope. This process may currently be occurring, and certainly during the active pyrite oxidation phases, Fe would have been highly soluble and mobile. Hence, the Bog Iron layer may have primarily formed during this time. The slope itself physically promotes down slope translocation of solutes, and water appears to move down slope at the base of the B1 horizon, which is likely continuous with the Bog Iron layer in the depression.

Additionally, the extreme enrichment of Fe (300,000 to 400,000 $\mu g\ g^{-1}$) indicates the ions were in solution prior to deposition, as appreciable levels of other elements that occur in soil would likely have decreased this level of purity *via* dilution. The plant opal layer, too, appeared relatively pure, present as a solid, whitish/yellowish layer within the Bog Iron.

Thus, the Bog Iron layer displays some unique characteristics that have not previously been described in acid sulphate soils. Despite its uniqueness, this layer was observed at other locations throughout the study area, in the depression at the bottom of slopes. It seems likely that the topography of the study area (moderate slopes on bedrock outcrops) is an important factor in the formation of this layer. Most acid sulphate soils (*e.g.*, Thailand, Vietnam) develop in marshlands and tidal zones, as the conditions for pyrite formation are often optimized in these areas (Section 2.6.5). Currently at the study site, the depression at the base of the slope connects to a narrow ravine where a shallow groundwater zone was observed at surface, and trees and shrubs were more abundant than

up slope. This ravine slopes to the southeast, where it opens to a cultivated agricultural field, approximately 1 km from the study site. A possible explanation for the formation of the Bog Iron layer is as follows:

1. Fe was translocated down slope in solution during and following pyrite oxidation. A closed basin might have existed at the bottom of the slope at the time, which would have prevented the Fe from being further transported down the ravine. The Fe precipitated out of solution and, slowly over time, the Bog Iron layer was developed. The Fe reactions might have been as follows:

   $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (soluble ferrous iron becomes oxidized)

   $2Fe^{3+} + \frac{1}{2}O_2 + H_2O \rightarrow 2FeOOH$ (ferric iron precipitates as goethite)

   $2FeOOH \rightarrow Fe_2O_3 + H_2O$ (goethite converts to hematite over time)

2. The 1 cm-thick plant opal layer observed within Bog Iron soil aggregates was pure and concentrated relative to most reports of plant opal. Many acid sulphate soils have a concentration of dissolved silica in soil solution sufficient to form opal phytoliths, but have not been reported in the amount observed in the Bog Iron layer. Thus, it is likely that the opal was concentrated, perhaps by fire, which would destroy plant tissues, but not the opal contained within. The opal may have then been transported into the depression and incorporated into the Bog Iron layer, likely by air deposition, as water or soil erosion would not result in the degree of purity that this layer exhibited. The mineralogy of the Bog Iron layer is consistent with this explanation, as hematite and maghemite (Figure 16; Figure A-1 and Figure A-2, Appendix) may be produced from goethite during a fire (Schwertmann and Fechter, 1984).
3. The closed basin eventually opens up, possibly as a result of water erosion, and a drainage path is developed, which slopes to the southeast. From that point, soluble ions are translocated down gradient in the narrow ravine that subsequently forms.

4.7. ARSENIC

4.7.1. Distribution in Boundary Soil Catena

Generally, As concentrations in all samples were high relative to the average As content of most soils, with values ranging from 10.0 μg g^{-1} (depression, A horizon) to 90.7 μg g^{-1} (depression, Bog Iron layer). Warren (1991) reported As concentrations of 4.9 μg g^{-1} in calcareous till from central Alberta; Dudas and Pawluk (1980) found 5.8 μg As g^{-1} Luvisolic C horizon from central Alberta; Taylor and McLellan (1985) report average As in shale as 6.6 μg g^{-1}. The average As concentration in samples analyzed for the current study was 34.6 μg g^{-1}. Elevated As concentrations in the Boundary Soils have been previously established (Dudas, 1984). Gustafsson and Tin (1994) reported similarly elevated As concentrations in acid sulphate soils from Vietnam (ranging from 6 to 41 μg As g^{-1}).

Arsenic generally increased in concentration down slope, except in the A horizon, where concentrations decreased down slope (Figure 22).

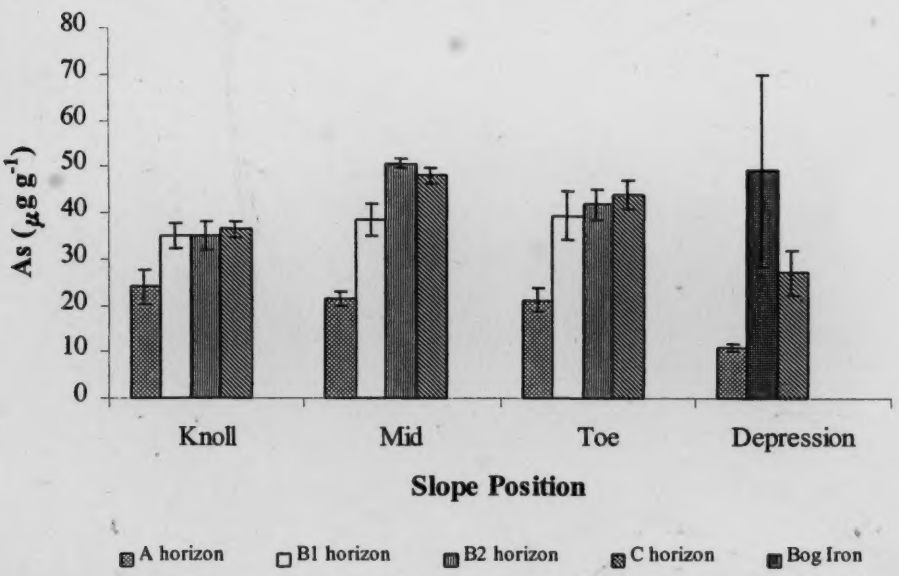

Figure 22. Average total arsenic concentrations in soil horizons along the slope.

These data show that, compared to the other soil horizons, As is least concentrated in the A horizon, with an average of 20.5 μg g^{-1}. The other three horizons have average As concentrations within 10 % of one another: 40.4 μg g^{-1} (B1), 42.4 μg g^{-1} (B2), and 38.8 μg g^{-1} (C). The locations of the highest average As concentrations are in the Bog Iron layer in the depression (49.2 μg g^{-1}) and the B2 horizon at mid slope (50.6 μg g^{-1}; Figure 22). Gustafsson and Tin (1994) also reported lowest As concentrations in the surface horizons of acid sulphate soils in Vietnam, with no distinct vertical As distribution throughout the solum.

There could be many reasons for low As concentrations in the A horizons on site. High microbial activity in the surface horizon, indicated by low redox potential (Figure 4) may result in the production of gaseous and volatile forms of As, which are released to the atmosphere (Ferguson and Gavis, 1972). Dudas (1984) postulated this as a possible explanation for observed lower levels of As in the A horizon. Organic matter additions from forest vegetation may cause dilution of As-enriched mineral soil. Dilution may be occurring in the Om/Ah horizon of the depression, where the lowest As concentrations were observed (Figure 22), along with the thickest organic matter-rich horizon (Table A-3, Appendix). Alternatively, the low As concentration in the Om/Ah horizon of the depression may be a result of the more abundant vegetation in the depression absorbing As through its roots. Additionally, As may have been eluviated from the A horizon to the lower solum along with the clay fraction, which is likely where most of the As resides.

4.7.2. Arsenic Geochemistry

Arsenic concentrations are relatively high in the Bog Iron layer (up to 90.7 μg g^{-1}), as would be expected with its high affinity for Fe (Bog Iron layer contains an average of 293,000 μg g^{-1} total Fe; Section 4.6.1). These As concentrations are lower than those measured in iron oxide-rich veinlets of the B and C horizons of Boundary Soils; concentrations up to 450 μg As g^{-1} were reported (Dudas, 1987). Such high concentrations indicate that mechanisms favouring the accumulation of As with Fe were occurring. In this study, As would be expected to follow Fe in its translocation to and accumulation in the Bog Iron layer in the depression. However, As is equally concentrated (average 50.6 μg As g^{-1}) in the B2 horizon at mid slope, with an average Fe

concentration of 53,000 μg g^{-1}, as it is in the Bog Iron layer (average 49.2 μg As g^{-1}), which has an average of 293,000 μg Fe g^{-1}. Perhaps conditions in the Bog Iron layer were different from those in veinlets, not optimizing arsenic precipitation and adsorption.

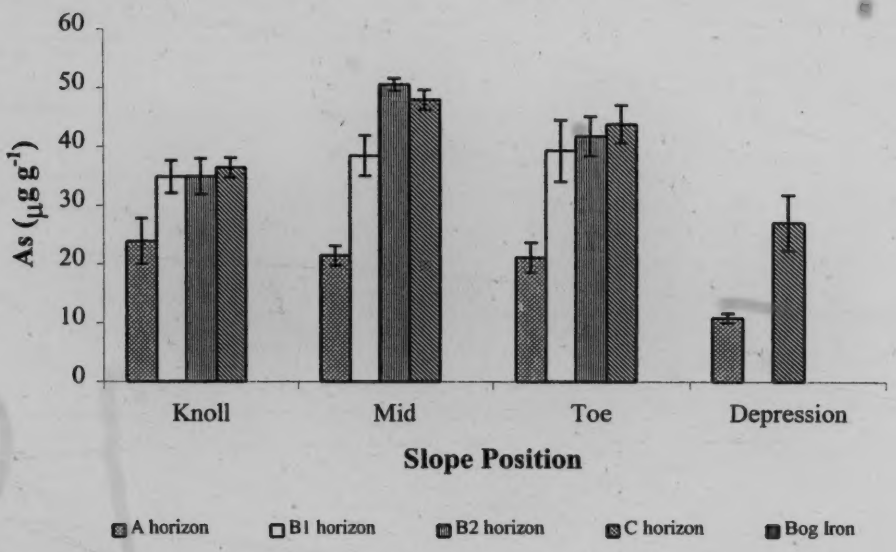

Figure 23. Average total arsenic concentrations (excluding Bog Iron samples) along the slope.

Viewed without the Bog Iron samples, As appears most highly concentrated in the lower B horizon at mid slope (Figure 23). High As in the B horizon at mid slope coincides with the highest clay content (Bulmer, 1987; Table A-2, Appendix) and Al concentration (Figure 12) in these soils. In view of the known association of As with iron oxides, this affiliation with clay would suggest that clays are coated with iron oxides, onto which As accumulates *via* sorption reactions. Aluminum, a major structural component of clays, and As are positively correlated (r = 0.29; Table 7). Graphically, this association is shown in Figure 24. Low Al and As in Om/Ah horizons in the depressional area (represented by circles on Figure 24), and low As/Al in the Bog Iron layer (represented by diamonds on Figure 24) detract from an otherwise even stronger correlation. Indeed, this correlation is statistically significant (r = 0.81; Table 8) when

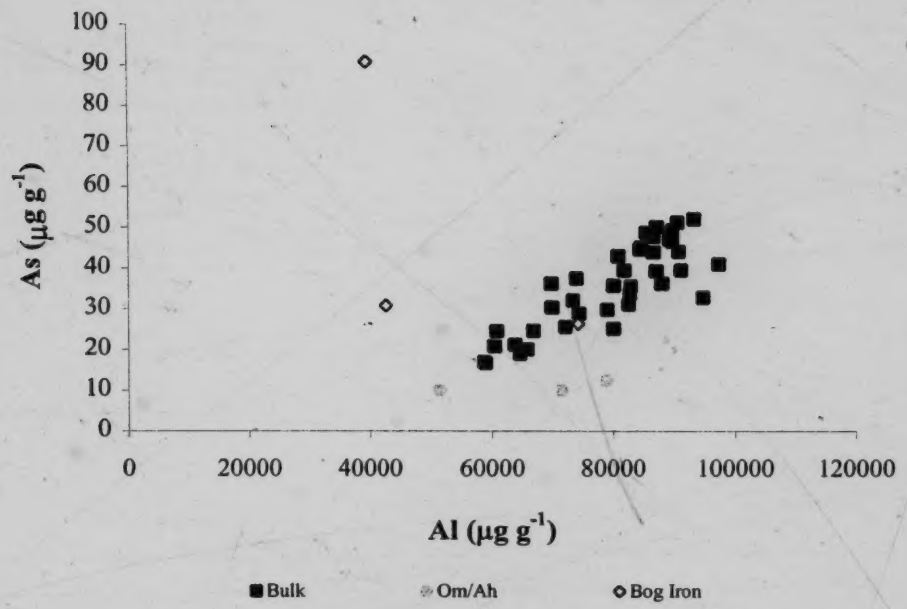

Figure 24. Aluminum versus arsenic.

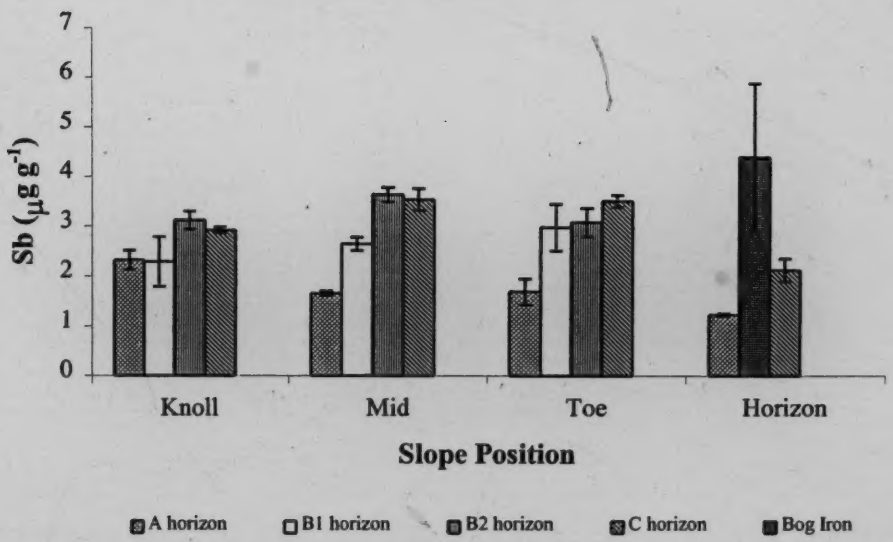

Figure 25. Average total antimony concentrations in soil horizons along the slope.

the Bog Iron samples are excluded from the data set, and is even higher (r = 0.84; Table 9) with Om/Ah samples removed from the data set. Without Bog Iron and Om/Ah samples, As and Al are in the same PCA groupings (Figures 9 and 10).

Antimony (Figure 25) exhibits nearly identical distribution as As (Figure 22), which is expected, as As and Sb are both Group V elements and, therefore, have similar chemical behaviour.

4.7.3. Speciation

The triangle on Figure 26 represents the average pH (4.16 in saturated paste extract) and the average Eh (510 mV; *pe* = 8.61) for the soil samples collected for this study. Thus, in an As-O-H system, soil conditions would favour As in the form of $H_2AsO_4^-$, an oxidized, As(V) oxyanion. Sadiq *et al.* (1983) report that 80 % of As is in the $H_2AsO_4^-$ form between pH 3 and 6, and that in soils with *pe* + pH above 9, arsenate species will be the most important. The soils studied had an average *pe* + pH of 12.8.

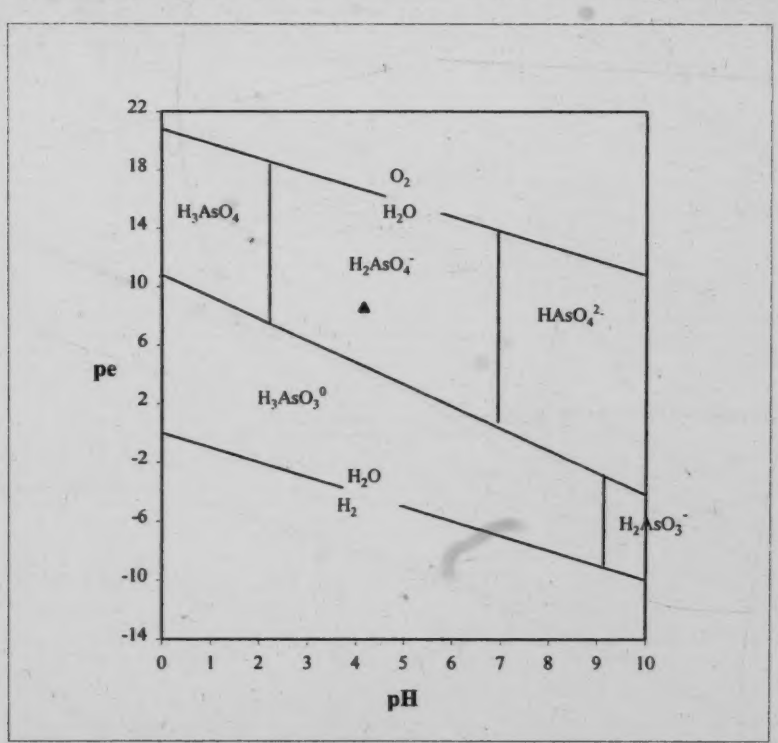

Figure 26. *pe*-pH diagram for As-O-H system.

4.8. SYNTHESIS

Arsenic is known to be strongly sorbed by iron oxides and greatly influenced by Fe chemistry in soil systems (Jacobs *et al.*, 1970; Livesey and Huang, 1981; Pierce and Moore, 1982; Dudas *et al.*, 1988; Cullen and Reimer, 1989; Masscheleyn *et al.*, 1991; McGeehan, 1996; Kabata-Pendias, 2001), and has previously been found in much higher concentrations in iron oxide veinlets in the Boundary Soils (up to 450 $\mu g\ g^{-1}$; Dudas, 1987) than in the bulk soil. In this study, the highest As concentration (90.7 $\mu g\ g^{-1}$) was found in a Bog Iron sample (Transect 1); however this concentration may be low, considering the abundance of iron oxides (300,000 to 400,000 $\mu g\ g^{-1}$). Additionally, As concentrations in the other two Bog Iron samples (26.3 $\mu g\ g^{-1}$, Transect 2; 30.7 $\mu g\ g^{-1}$, Transect 3) are lower than those of several other samples collected from the site (Table A-4, Appendix), and the average As concentration in the B2 horizon at mid slope (with 53,000 μg Fe g^{-1}) was equal to that in the Bog Iron layer (with 293,000 μg Fe g^{-1}).

In these soils, Fe appears to have become soluble during pyrite oxidation and was translocated down slope, precipitating from solution into an aqueous environment. Arsenic would also have been soluble under the acidic conditions created by pyrite oxidation. Although As is strongly attracted to iron oxides, and thereby normally accumulates with Fe, in this study, As concentrations were not as high as expected in the Fe-rich Bog Iron layer.

Low pH conditions like those that develop during pyrite oxidation (< 3.5) allow for the solubility of many elements and the dissolution of many minerals. Silicate minerals dissolve below pH 4 (Courchesne and Hendershot, 1989). Evidence of this was observed in the Boundary Soils, with the presence of plant opal (amorphous hydrous silica) and abnormally high levels of Al in groundwater. Sulphate would have been highly concentrated in soil solution during pyrite oxidation, since it is one of the primary products of the oxidation reactions. Sulphate has been observed to be an effective competitor for anion adsorption sites in soils (Courchesne and Hendershot, 1989; Fasth *et al.*, 1991; Wilkie and Hering, 1996; Meng *et al.*, 2000). Sulphate and arsenate are both oxyanions in soil solution, and iron oxides and hydroxides are amphoteric minerals, which are positively charged at pH values below their point of zero charge (*e.g.*, pH of 7

for hematite; Xu *et al.*, 1991). At the pH levels that occur in the Boundary Soils, iron oxides would be positively charged, and the abundance of these charged sites would increase with decreasing pH to a point where the sorptive minerals themselves dissolve (around pH 3.5; Carson *et al.*, 1982). Therefore, for a large proportion of the lifetime of the Boundary Soils, conditions have likely been optimal for anion adsorption by iron oxides.

Wilkie and Hering (1996) observed SO_4^{2-} to cause a decrease in As sorption onto hydrous ferric oxide from pH 4 to 7. This was enhanced as both SO_4^{2-} and As concentrations increased. In addition to occupying sorption sites, SO_4^{2-} may combine with arsenate in solution (forming $SAsO_4^{2-}$) and prevent As adsorption (Meng *et al.*, 2000). Meng *et al.* (2000) also reported adverse effects on As(III) and As(V) sorption due to the presence of SO_4^{2-}, CO_3^{2-}, and natural organic matter. Concentrations of SO_4^{2-} in Boundary Soil solution would be much higher than As concentrations, even during active pyrite oxidation, due to the abundance of sulphate in parent minerals. Therefore, mass action, plus the behaviours described above, would allow relatively little As sorption.

Thus, it seems possible that during active pyrite oxidation, when acidity was high and many elements were soluble, As was out-competed for iron oxide sorption sites, likely by sulphate. Additionally, as pH increased post pyrite oxidation, anion adsorption capacity of the amphoteric minerals would have decreased, thus potentially releasing sorbed As to solution. Since As is currently present in extremely low concentrations in groundwater on site, perhaps it remained in solution and continued to be transported with groundwater down gradient. According to aerial photographs and field observations, this would be to the southeast, towards an agricultural area.

5. SUMMARY AND CONCLUSIONS

Arsenic concentrations in the soils of this study ('Boundary' soil series) were high relative to other Alberta soils, and exhibited highest concentrations in the Bog Iron layer in the depression and in the lower B horizon at mid slope. Thermodynamic calculations indicate that As is likely present in the soil solution as the As(V) oxyanion, $H_2AsO_4^-$. Iron and As would likely have been soluble due to the extreme acidity created during acid sulphate soil genesis. Since As did not accumulate with Fe at the base of the slope to the degree expected, it is possible that competing and abundant anions, such as sulphate, occupied most of the available surface sites on the Fe minerals. Additionally, the rise in pH that occurs in post-active acid sulphate soils would have decreased the anion adsorption capacity of As-sorbing minerals, such as iron oxides, and may have resulted in release of sorbed As to solution. Since As concentrations in groundwater are very low, perhaps the soluble As continued to migrate down gradient to the southeast.

Thus, both parts of the hypothesis, which postulated down slope movement of As and increased concentrations of As in soil and/or groundwater down slope, are unresolved. Arsenic was highly concentrated in the Bog Iron layer of the depression, which would be consistent with down slope translocation; however, concentrations were equally high in the lower B horizon at mid slope. Arsenic concentrations in soil were higher than average; those in groundwater were very low, but were likely high at the time of pyrite oxidation. Since that time, the arsenic may have been transported away from the study site.

The results of this study indicate that pH exerts the most influence over As behaviour in the soil system studied. Although Eh and iron oxide chemistry are also known to be influential in As chemistry, the extreme acidic conditions that develop during pyrite oxidation may supersede these factors. The low pH maintains the Eh at relatively high voltage, and causes dissolution of soil constituents, resulting in high concentrations of competing ions for sorption sites on iron oxides.

An Fe-rich layer (300,000 to 400,000 $\mu g\ Fe\ g^{-1}$), called 'Bog Iron', was present at the study site at the bottom of the slope in the depression. Concentrations of many elements were unusual (either significantly enriched or depleted) in this layer compared to the other soil samples. As a consequence, these samples skewed the data, so statistical

analyses were re-calculated excluding the Bog Iron samples. Iron, As, and Sb exhibited peak concentrations in this layer. However, even greater concentrations of As were expected due to the abundance of iron oxides. Iron and As were not significantly correlated. Evidence suggests that Fe was solubilized and translocated down slope over many years, precipitating at the bottom of the slope. Hematite is the dominant Fe mineral in this layer. A seemingly pure deposit of plant opal (amorphous hydrous silica) was present in the Bog Iron layer.

An Fe-rich layer like the Bog Iron layer has not been previously described in acid sulphate soils. This may be because acid sulphate soils often develop in flat, marshy or tidal areas that do not have the topography that would enhance down slope movement and accumulation of constituents. Similar Fe-rich layers were observed in other depressional locations in the study area.

Bromine, Co, Mn and Na were found to be low in Boundary Soils relative to other Alberta soils. Arsenic, Ce, Cr, La, Rb, Sm, Sc, Th, U, V, and Zn were relatively enriched. Elevated levels of arsenic in these soils have been previously reported.

Previous studies have identified kaolinite and micas as the primary silicate minerals present in the soils. Smectites have also been identified. Jarosite and natrojarosite, common by-products of pyrite oxidation, are present in the lower solum.

Calcium, Al, Mg, Fe, and Mn concentrations in groundwater at the site were higher than those of average Alberta groundwater; Na, As, and Mo concentrations were low relative to average Alberta groundwater; and K and Se concentrations were comparable to average Alberta groundwater. Sulphate is the dominant anion in groundwater of the study area.

Characterization of local and regional groundwater chemistry and flow in the area of the site would provide further insight into the distribution and fate of As. Focus on the groundwater chemistry down gradient of the site to the southeast in the agricultural fields is recommended.

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APPENDIX

Table A-1. Laboratory-measured parameters.

Sample Name	Water Content	Saturation	pH (sat paste extract)	pH ($CaCl_2$)	Redox Potential (sat paste)	pe*	Electrical Conductivity (sat paste extract)
	(%)	(%)	(no units)	(no units)	(mV)	(no units)	(dS m^{-1})
T1 Ah K	21.9	53.8	4.89	3.80	451	7.62	0.321
T1 Bfj1 K	24.7	67.6	5.88	3.70	521	8.8	0.162
T1 Bfj2 K	23.1	83.8	6.02	3.46	636	10.7	0.176
T1 C K	22.9	82.7	5.16	3.27	671	11.3	0.190
T1 Ahj M	34.8	50.2	4.56	3.68	- 201	-3.4	0.867
T1 Bfj1 M	26.3	62.7	4.63	3.66	515	8.7	0.425
T1 Bfj2 M	30.7	80.7	5.13	3.46	637	10.8	0.318
T1 C M	30.7	80.9	4.04	3.32	633	10.7	0.262
T1 Ah T	28.3	49.3	4.47	3.88	-201	-3.4	0.460
T1 Bfj1 T	28.2	67.9	4.29	3.58	442	7.5	1.31
T1 BgnBfj2 T	37.7	80.7	4.35	3.33	609	10.3	1.38
T1 Cg T	51.9	66.6	3.17	3.17	618	10.4	1.70
T1 Om & Ah D	222	157	4.03	3.84	281	4.7	1.77
T1 Bog Iron D	43.3	73.8	4.08	4.00	488	8.2	1.63
T1 Cg D	76.9	66.8	3.76	3.50	670	11.3	1.31
T2 Ah K	38.8	66.6	4.11	3.77	-165	-2.8	0.377
T2 Bfj1 K	32.3	72.3	4.41	3.59	433	7.3	0.124
T2 Bfj2 K	32.4	80.1	4.00	3.47	541	9.1	0.111
T2 C K	25.1	71.5	4.13	3.30	661	11.2	0.106
T2 Ah M	46.9	78.4	4.41	3.87	-194	-3.3	0.442
T2 Bfj1 M	27.1	56.2	4.63	3.66	-208	-3.5	0.142
T2 Bfj2 M	27.2	64.2	4.48	3.51	561	9.5	0.115
T2 C M	26.8	66.6	7.15	3.37	592	10.0	0.163
T2 Ah T	34.3	82.7	3.89	3.59	470	7.9	0.867
T2 Bg1 T	23.1	59.2	3.71	3.45	582	9.8	1.20
T2 Bg2 T	32.7	66.5	3.52	3.33	609	10.3	1.27
T2 Cg T	37.8	79.8	3.48	3.24	672	11.4	1.13
T2 Om, Oh, Ah D	88.1	89.1	3.99	3.65	452	7.6	1.38
T2 Bog Iron D	92.5	89.8	4.06	3.86	458	7.7	1.27
T2 Cg D	47.2	66.0	3.45	3.23	635	10.7	1.10
T3 Ah K	27.8	N/A	4.02	3.44	436	7.4	0.230
T3 Bfj1 K	23.8	N/A	4.13	3.55	473	8.0	0.096
T3 Bfj2 K	24.8	N/A	4.03	3.45	539	9.1	0.078
T3 C K	21.6	N/A	4.11	3.33	598	10.1	0.081
T3 Ah M	43.2	N/A	4.38	4.04	315	5.3	0.354
T3 Bfj1 M	22.7	N/A	4.23	3.62	495	8.4	0.124
T3 Bf2 M	25.6	N/A	4.19	3.46	564	9.5	0.092
T3 C M	25.1	N/A	4.32	3.32	620	10.5	0.131
T3 Ah T	32.6	62.7	3.95	3.60	470	7.9	0.442
T3 Bfjg1 T	26.9	78.3	3.57	3.34	578	9.8	0.884
T3 Bfjg2 T	39.8	82.0	3.43	3.23	630	10.6	1.10
T3 Cg T	44.0	90.5	3.39	3.20	667	11.3	0.955
T3 Om & Ah D	196	224	3.64	3.35	465	7.9	2.05
T3 Bog Iron D	82.9	82.1	3.62	3.48	503	8.5	1.49
T3 Cg D	44.7	69.5	3.32	3.31	614	10.4	1.10

Notes: N/A = not available
* calculated from measured redox potential [pe = Eh (mV) *59.2]

Table A-2. Various physical and chemical parameters of the Boundary Soils.

Sample	Horizon	Depth (cm)	Mineral Type	Phyllosilicate Type	Extractable Fe and Al (%)				pH ($CaCl_2$)	Total CEC ($cmol\ kg^{-1}$)
					Fe-ox	Fe-di	Al-ox	Al-di		
A1(upper slope)	Ahe	0-4	—	hydrous mica	0.60	3.90	0.29	0.39	3.9	23.5
A2	Btjf1	4-26	—	hydrous mica	0.86	4.67	0.30	0.38	3.5	23.2
A3	Btfj2	26-43	goethite, hematite	mica	1.62	6.92	0.17	0.20	3.2	19.1
A4	BC	43-58	jarosite	hydrous mica	0.41	3.26	0.14	0.18	3.1	19.7
A5	C1	58-75	—	mica, kaolinite	0.23	4.00	0.14	0.18	3.1	18.1
A6	C2	75-95	—	mica, kaolinite	0.19	3.82	0.13	0.16	3.1	16.7
A7	C3	95-110	natrojarosite	mica, kaolinite	0.28	5.66	0.12	0.16	3.1	17.8
B1(mid slope)	Ahe	0-4	—	—	0.66	3.18	0.25	0.25	4.0	23.5
B2	Btfj1	4-18	—	—	0.91	4.02	0.28	0.36	3.7	23.5
B3	Btfj2	18-36	—	—	0.93	4.17	0.22	0.25	3.5	23.2
B4	BC	36-55	—	—	0.37	3.32	0.19	0.19	3.4	22.3
B5	C1	55-75	—	—	0.22	4.32	0.16	0.17	3.3	20.4
B6	C2	75-95	—	—	0.21	4.18	0.17	0.15	3.4	21.6
B7	C3	95-105	—	—	0.37	3.97	0.17	0.19	3.3	21.6
C1(lower-mid slope)	Ahe	0-5	—	—	0.77	2.59	0.24	0.21	4.0	22.5
C2	Btfj1	5-15	—	—	0.76	3.38	0.42	0.40	3.9	23.8
C3	Btfj2	15-30	—	—	0.74	3.57	0.35	0.37	3.9	21.3
C4	Btfj3	30-50	—	—	1.20	3.76	0.27	0.31	3.6	21.4
C5	BC	50-65	—	—	0.56	3.24	0.21	0.26	3.4	18.7
C6	C1	65-80	—	—	0.31	2.87	0.17	0.17	3.4	17.3
C7	C2	80-105	—	—	0.30	3.29	0.17	0.17	3.4	17.5
D1(lower slope)	IAhe	0-6	—	—	0.57	1.56	0.21	0.19	3.9	22.5
D2	IBtfj1	6-16	—	—	0.93	2.21	0.41	0.37	4.0	21.2
D3	IBtfj2	16-27	—	—	1.07	2.81	0.56	0.51	4.0	19.9
D4	IIBtfj	27-40	—	—	0.78	3.06	0.29	0.27	3.7	19.7
D5	IIBC	40-60	—	—	0.51	3.47	0.19	0.19	3.4	17.4
D6	IIC1	60-83	—	—	0.52	3.98	0.17	0.17	3.3	18.1
D7	IIC2	83-100	—	—	0.57	4.42	0.13	0.13	3.3	17.8

Table A-2. Various physical and chemical parameters of the Boundary Soils.

Sample	Horizon	Depth (cm)	Mineral Type	Phyllosilicate Type	Extractable Fe and Al (%)				pH ($CaCl_2$)	Total CEC ($cmol\ kg^{-1}$)
					Fe-ox	Fe-di	Al-ox	Al-di		
Bd4b (knoll top)	Aej	0-8	—	smectite, muscovite, kaolinite[e]	—	—	—	—	—	—
Bd4c	AB	8-24	goethite, hematite, lepidocrocite[e]	smectite, muscovite, kaolinite[e]	—	—	—	—	—	—
Bd4d	Bftj	24-44	goethite, hematite, lepidocrocite[e]	smectite, muscovite, kaolinite[e]	—	—	—	—	—	—
Bd4e	C1	44-70	weathered pyrite[c]	smectite, muscovite, kaolinite[e]	—	—	—	—	—	—
Bd4f	C2	70-100	weathered pyrite, natrojarosite[e]	smectite, muscovite, kaolinite[e]	—	—	—	—	—	—
Bd1b, Bd2a (well-drained)	Aej	—	—	—	—	—	—	—	—	—
Bd1c, Bd2b	Bftj	—	—	—	—	—	—	—	—	—
Bd1d	Bf	—	—	—	—	—	—	—	—	—
Bd1e, Bd2c	BC	—	—	—	—	—	—	—	—	—
Bd1f, Bd2d	C	—	—	—	—	—	—	—	—	—
	Ahe	—	—	vermiculite, kaolinite, mica[d]	—	—	—	—	—	—
	E	—	—	—	—	—	—	—	—	—
	BE	—	—	—	—	—	—	—	—	—
	Bt1	—	goethite[d]	mica, kaolinite[d]	—	—	—	—	—	—
	Bt2	—	—	—	—	—	—	—	—	—
	BC	—	natrojarosite[d]	mica, kaolinite[d]	—	—	—	—	—	—
	C	—	natrojarosite[d]	mica, kaolinite[d]	—	—	—	—	—	—
Natrojarosite	—	—	—	—	—	—	—	—	—	—
Iron Oxide Veinlets	—	—	—	—	0.56-10[b]	5.8-15[b]	0.13-0.68[b]	0.10-0.89[b]	—	—

Table A-2. Various physical and chemical parameters of the Boundary Soils.

Sample	Horizon	Depth (cm)	Base Saturation (%)	Organic C (%)	Sand (%)	Silt (%)	Clay (%)	Bulk Density ($Mg\ m^{-3}$)	As ($mg\ g^{-1}$)	As ($\mu g\ g^{-1}$)			
										total silt	fine silt	total clay	fine clay
A1(upper slope)	Ahe	0-4	23.4	2.38	—	—	—	0.65	—	—	—	—	—
A2	Btjf1	4-26	2.6	0.83	—	—	—	1.15	—	—	—	—	—
A3	Btfj2	26-43	2.1	0.50	—	—	—	1.24	—	—	—	—	—
A4	BC	43-58	2.0	—	—	—	—	—	—	—	—	—	—
A5	C1	58-75	2.2	—	—	—	—	1.41	—	—	—	—	—
A6	C2	75-95	2.4	—	—	—	—	—	—	—	—	—	—
A7	C3	95-110	1.7	—	—	—	—	—	—	—	—	—	—
B1(mid slope)	Ahe	0-4	32.8	1.78	2.4	37.6	60.0	—	—	—	—	—	—
B2	Btfj1	4-18	5.5	0.79	0.3	30.5	69.2	—	—	—	—	—	—
B3	Btfj2	18-36	4.3	0.58	0.1	32.8	67.1	—	—	—	—	—	—
B4	BC	36-55	3.1	—	0.1	40.2	59.7	—	—	—	—	—	—
B5	C1	55-75	2.5	—	0.1	42.8	57.1	—	—	—	—	—	—
B6	C2	75-95	1.9	—	0.0	44.6	55.1	—	—	—	—	—	—
B7	C3	95-105	1.9	—	0.1	45.8	54.1	—	—	—	—	—	—
C1(lower-mid slope)	Ahe	0-5	35.1	2.42	2.4	44.1	53.5	—	—	—	—	—	—
C2	Btfj1	5-15	9.7	1.50	1.2	38.7	60.1	—	—	—	—	—	—
C3	Btfj2	15-30	5.6	0.94	0.3	32.1	67.6	—	—	—	—	—	—
C4	Btfj3	30-50	4.2	0.60	0.1	32.8	67.1	—	—	—	—	—	—
C5	BC	50-65	3.2	—	0.1	39.5	60.4	—	—	—	—	—	—
C6	C1	65-80	2.9	—	0.0	43.6	56.4	—	—	—	—	—	—
C7	C2	80-105	2.3	—	0.0	45.5	54.5	—	—	—	—	—	—
D1(lower slope)	IAhe	0-6	32.9	3.91	—	—	—	0.91	—	—	—	—	—
D2	IBtfj1	6-16	12.7	2.23	—	—	—	—	—	—	—	—	—
D3	IBtfj2	16-27	8.0	1.38	—	—	—	1.38	—	—	—	—	—
D4	IIBtfj	27-40	7.6	0.64	—	—	—	1.36	—	—	—	—	—
D5	IIBC	40-60	8.0	—	—	—	—	—	—	—	—	—	—
D6	IIC1	60-83	9.9	—	—	—	—	1.40	—	—	—	—	—
D7	IIC2	83-100	11.8	—	—	—	—	—	—	—	—	—	—

Table A-2. Various physical and chemical parameters of the Boundary Soils.

Sample	Horizon	Depth (cm)	Base Saturation (%)	Organic C (%)	Sand (%)	Silt (%)	Clay (%)	Bulk Density (Mg m^{-3})	As (mg g^{-1})	As (µg g^{-1})			
										total silt	fine silt	total clay	fine clay
Bd4b (knoll top)	Aej	0-8	—	—	—	—	32[b]	—	8.0[b]	—	—	—	—
Bd4c	AB	8-24	—	—	—	—	59[b]	—	23[b]	—	—	—	—
Bd4d	Bftj	24-44	—	—	—	—	68[b]	—	33[b]	—	—	—	—
Bd4e	C1	44-70	—	—	—	—	61[b]	—	40[b]	—	—	—	—
Bd4f	C2	70-100	—	—	—	—	58[b]	—	35[b]	—	—	—	—
Bd1b, Bd2a (well-drained)	Aej	—	—	—	—	—	—	—	—	1.2[b], 2.4[b]	1.3[b], 2.3[b]	9.5[b], 13[b]	11[b], 19[b]
Bd1c, Bd2b	Bftj	—	—	—	—	—	—	—	—	5.4[b], 7.4[b]	6.0[b], 6.9[b]	20[b], 21[b]	29[b], 24[b]
Bd1d	Bf	—	—	—	—	—	—	—	—	14[b]	20[b]	47[b]	50[b]
Bd1e, Bd2c	BC	—	—	—	—	—	—	—	—	11[b], 6.0[b]	13[b], 7.9[b]	47[b], 26[b]	54[b], 40[b]
Bd1f, Bd2d	C	—	—	—	—	—	—	—	—	8.8[b], 5.7[b]	9.2[b], 8.6[b]	42[b], 34[b], 43[e]	51[b], 49[b]
	Ahe	—	—	1.65[d]	—	—	—	—	—	—	—	—	—
	E	—	—	—	—	—	—	—	7.0[e]	—	—	—	—
	BE	—	—	—	—	—	—	—	8.0[e]	—	—	—	—
	Bt1	—	—	—	—	—	—	—	23[e]	—	—	—	—
	Bt2	—	—	—	—	—	—	—	33[e]	6.0[e]	7.9[e]	38[e]	—
	BC	—	—	—	—	—	—	—	40[e]	—	—	—	—
	C	—	—	0.50[d]	—	—	—	—	33[e]	—	—	—	—
Natrojarosite	—	—	—	—	—	—	—	—	41[e], 61[e]	—	—	—	—
Iron Oxide Veinlets	—	—	—	—	—	—	—	—	290[e], 30-450[b], 180-400[e]	—	—	—	—

Notes:
[a]from Dudas (1984)
[b]from Dudas (1987)
[c]from Dudas, Warren, and Spiers (1988)
[d]from Pawluk and Dudas (1978)
[e](or no superscript) from Bulmer (1987)

V samples = samples of vein-like accumulations of iron oxyhydroxides
Fe-ox = acid ammonium oxalate-extractable iron
Fe-di = sodium-dithionite-citrate-bicarbonate extractable iron
total silt = 0.05-0.002 mm; fine silt = 0.005-0.002 mm
total clay = < 0.002 mm; fine clay = < 0.0005 mm

Table A-3. Soil profile descriptions.

Transect	Slope Position	Sample Name	Horizon	Depth (cm)	Description
1	Knoll	T1 Ah K	Ah	0-8	brown (7.5 YR 4/3) and very dark grey (3/1) flecks of organic matter; silty clay; lots of organic matter; many fine and few medium roots; dry.
1	Knoll	T1 Bfj1 K	Bfj1	8-28	brown (7.5 YR 4/4), uniform color; clay; few fine (2mm) roots; dry.
1	Knoll	T1 Bfj2 K	Bfj2	28-58	strong brown (7.5 YR 4/6) with slight grey tinge (4/10 Y); clay; few fine and medium roots; dry.
1	Knoll	T1 C K	C	58+	greenish grey (5/5 G; gleyed), dark greenish grey (4/5 GY) and strong brown (7.5 YR 4/6; mottled); clay; few fine roots; dry.
1	Mid	T1 Ahj M	Ahj	0-8	dark brown (10 YR 3/3) to dark yellowish brown (10 YR 3/4); silty clay; lots organic matter; many fine and medium roots; dry.
1	Mid	T1 Bfj1 M	Bfj1	8-30	dark brown (7.5 YR 3/3 and 3/4); silty clay to clay; semi-decomposed organic matter; many fine and few medium roots; dry.
1	Mid	T1 Bfj2 M	Bfj2	30-68	brown (7.5 YR 4/4) to strong brown (7.5 YR 4/6); clay; few fine roots; dry.
1	Mid	T1 C M	C	68+	dark greenish grey (4/5 GY, 4/10 GY) gleying and olive yellow (2.5 Y 6/8) to light olive brown (2.5 Y 5/6) mottling; clay; few fine roots, one medium root; dry.
1	Toe	T1 Ah T	Ah	0-10	very dark greyish brown (10 YR 2/2); fine and medium granular and fine subangular blocky structure; silty clay; abundant, fine and medium roots.
1	Toe	T1 Bfj1 T	Bfj1	10-40	brown to dark brown (7.5 YR 4/4 to3/4), clay; medium to fine granular and medium subangular blocky structure; abundant, fine to medium roots.
1	Toe	T1 Bfj2 T	Bfj2	40-85 V	dark yellowish brown (10 YR 3/4 to 3/6), clay to hard clay; fine and medium, granular and medium subangular structure; few medium and large roots.
1	Toe	T1 Cg T	Cg	85+	dark yellowish brown (10 YR 4/6) with 5/5 B gleyed patches; clay to hard clay; soaking wet.
1	Depression	T1 Om & Ah D	Om, Ah	0-20 V	dark reddish brown (5 YR 2.5/2) to black (5 YR 2.5/1) with flecks of 5 YR 3/4; silty clay; abundant, fine and medium roots; semi-decomposed wood chunks; wet.
1	Depression	T1 Bog Iron D	Bog Iron	20-30	very dusky red (2.5 YR 2.5/2) (main color), dark red (2.5 YR 3/6; brighter red inside large aggregates), and a layer of pale yellow (2.5 Y 7/3) (plant opal?); silty clay (more clay); fine to medium granular structure; abundant fine and medium roots; wet.
1	Depression	T1 Cg D	Cg	30-100	very dark grey (10 YR 3/1) with some 4/10 Y gleying; hard clay; few, fine roots; wet.
2	Knoll	T2 Ah K	Ah	0-6	dark brown (7.5 YR 3/3 to 3/4) with black flecks (7.5 YR 2.5/1); silty clay (lots clay); abundant, fine and medium roots; one large twig (1 cm diameter, 10 cm long); dry to moist.
2	Knoll	T2 Bfj1 K	Bfj1	6-30	brown (7.5 YR 4/4) to dark brown (7.5 YR 3/4); clay to hard clay; abundant, fine, medium, and large (0.5 cm diameter) roots; dry to moist.
2	Knoll	T2 Bfj2 K	Bfj2	30-65	strong brown (7.5 YR 4/6) to yellowish red (5 YR 4/6) with grey (5/10 Y to 4/10 Y); clay; few, fine to medium roots; dry to moist.
2	Knoll	T2 C K	C	65+	dark greenish grey (4/10 Y) with some yellowish brown (10 YR 5/6) in center of clumps; hard clay; few, fine and medium roots; moist.
2	Mid	T2 Ah M	Ah	0-10	very dark brown (10 YR 2/2) and black (10 YR 2/1); silty clay with lots of organic matter; abundant, fine and medium roots (mostly fine); some semi-decomposed wood and leaves; fairly dry.
2	Mid	T2 Bfj1 M	Bfj1	10-35	brown (7.5 YR 4/4); clay; few, fine roots; small about of leaf/wood litter; fairly dry.
2	Mid	T2 Bfj2 M	Bfj2	35-70	dark yellowish brown (10 YR 4/4 to 4/6); clay to hard clay; few, fine roots; moist.

Table A-3. Soil profile descriptions.

Transect	Slope Position	Sample Name	Horizon	Depth (cm)	Description
2	Mid	T2 C M	C	70+	dark greenish grey (4/5 GY, 4/10 GY) gleying and olive yellow (2.5 Y 6/8) to light olive brown (2.5 Y 5/6) mottling; clay; few fine roots, one medium root; dry.
2	Toe	T2 Ah T	Ah	0-12	very dark brown (7.5 YR 2.5/2 to 2.5/3); silty clay; lots organic matter (decomposed and semi-decomposed wood and leaves); abundant, fine and medium roots; dry to moist.
2	Toe	T2 Bg1 T	Bg1	12-45 V	brown (7.5 YR 4/3 to 4/4); clay; many, fine roots and few, medium roots; some leaves; dry to moist.
2	Toe	T2 Bg2 T	Bg2	45-85	yellowish brown (10 YR 5/4) to brown (7.5 YR 4/4) (grey inside clumps 7.5 YR 5/1); clay to hard clay; few, fine roots and many, medium roots; moist.
2	Toe	T2 Cg T	Cg	85	dark yellowish brown (10 YR 4/4) with brighter brown (dark yellowish brown 10 YR 4/6) and strong brown (7.5 YR 4/6), with greyish brown (10 YR 5/2) inside clumps; clay to hard clay; few, medium roots; moist.
2	Depression	T2 Om,Oh,Ah D	Om,Oh,Ah	0-18 V	black inside clumps (10 YR 2/1) to dark/very dark greyish brown (10 YR 4/2, 3/2) and bits of dark reddish brown (5 YR 3/3); silty clay; abundant organic matter (black); many, fine roots, few large roots; wet; boggy odor.
2	Depression	T2 Bog Iron D	Bog Iron	18-30	yellowish red (5 YR 4/6), reddish brown (5 YR 4/4), and dark reddish brown (5 YR 3/5 and 3/4) with some darker areas (of organic matter 5 YR 3/1 and 2.5/1); silty clay; lots organic matter; many, fine roots; wet.
2	Depression	T2 Cg D	Cg	30-100	very dark grey (2.5 Y 3/1) to black (2.5 Y 2.5/1) with yellowish brown bits (10 YR 5/6, 5/8); hard clay; no roots; moist.
3	Knoll	T3 Ah K	Ah	0-10	very dark brown (10 YR 2/2) with dark yellowish brown flecks (10YR 4/6); silty clay (lots clay); some semi-decomposed leaves and OM; abundant small and medium (up to 5 mm diameter) roots; stony; dry to moist.
3	Knoll	T3 Bfj1 K	Bfj1	10-35	strong brown (7.5 YR 4/6); clay; many fine and few medium roots, some pieces of leaves, one small (< 1cm diameter) rock; dry to moist.
3	Knoll	T3 Bfj2 K	Bfj2	35-70	strong brown (7.5 YR 4/6); clay; few medium and fine roots; few leaf bits; stony; dry to moist.
3	Knoll	T3 C K	C	70+	dark greenish grey (chart 1 for gley 4/1, whole range) with light yellowish brown (10 YR 5/6 to 5/88) throughout; clay to hard clay; dry to moist.
3	Mid	T3 Ah M	Ah	0-8	very dark brown to black (10YR 2/2 to 2/1); silty clay; large amounts of organic matter, semi-decomposed wood, leaves; abundant small and medium roots; dry to moist.
3	Mid	T3 Bfj1 M	Bfj1	8-40	dark brown (7.5 YR 3/4) to strong brown (7.5 YR 4/6); clay; few fine roots; dry to moist.
3	Mid	T3 Bfj2 M	Bfj2	40-75	light olive brown (2.5 Y 5/4, 5/6) to olive brown (2.5 Y 4/4) due to this layer being a cross between Bfj1 and C; clay; few fine to medium roots; a couple of yellow stones (~ 1 cm dia); dry to moist.
3	Mid	T3 C M	C	75+	olive brown (2.5 Y 4/4) and dark greenish grey (chart 1 for gley 4/10 Y) mixture; clay to hard clay; few fine roots; dry to moist (large, baseball-sized aggregates); a couple of yellow stones, as above.
3	Toe	T3 Ah T	Ah	0-8	very dark brown (10 YR 2/2); silty clay; some organic matter and semi-decomposed wood and leaves; abundant small and medium, and few large (8 mm diameter) roots; dry.
3	Toe	T3 Bfjg1 T	Bfjg1	8-40	dark yellowish brown (10 YR 4/4); clay; some small and medium roots; dry to moist.

Table A-3. Soil profile descriptions.

Transect	Slope Position	Sample Name	Horizon	Depth (cm)	Description
3	Toe	T3 Bfjg2 T	Bfjg2	40-80 ▽	greenish grey gleying (5/5 GY); dark yellowish brown mottling (10YR 4/6, dark yellowish brown); clay to hard clay; few fine roots; dry to moist.
3	Toe	T3 Cg T	Cg	80+	greenish grey gleying (5/10 Y); olive brown (2.5 Y 4/4) and dark yellowish brown (10 YR 4/6) mottling; clay to hard clay; one fine root; bits of yellow stone/mineral; moist.
3	Depression	T3 Om,Ah D	Om,Ah	0-22 ▽	black organic matter (10 YR 2/1 and even more black) to very dark brown (10 YR 2/2); silty clay; large abundance of organic matter, semi-decomposed leaves and wood; one small herb (*Cornus canadensis*?); many small and medium roots; moist to wet.
3	Depression	T3 Bog Iron D	Bog Iron	22-32	very dark red (2.5 YR 2.5/3) with some brighter (2.5 YR 4/8, dark red) colours inside clumps, and black (10 YR 2/1) organic matter (< 5 %); silty clay; many fine roots; wet to saturated.
3	Depression	T3 Cg D	Cg	32-100	greenish grey gleying (5/10 BG), dark yellowish brown mottling (10 YR 4/6, 4/4 on outside of clumps); clay to hard clay; one or two fine roots; moist.

Notes: ▽ = evidence of upper groundwater zone (i.e., wet to saturated soil) observed
Colour descriptions are of moist soil.

Table A-4. Total elements by NAA.

Lab Sample ID	Field Sample ID	Al	Uncertainty	As	Uncertainty	Br	Uncertainty	Ce	Uncertainty	Co	Uncertainty	Cr	Uncertainty	Fe	Uncertainty
		(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})
PB-16	T1 Ah K	60800	600	24.4	0.6	2.0	0.3	66	2	6.2	0.7	105	5	28800	700
PB-17	T1 Bfj1 K	80000	600	35.6	0.3	2.5	0.2	72	2	3.2	0.6	101	4	35100	1000
PB-18	T1 Bfj2 K	94700	700	32.8	0.3	2.6	0.2	78	3	2.7	0.7	118	5	32600	1000
PB-19	T1 C K	91000	600	39.4	0.4	2.4	0.2	90	2	2.2	0.7	131	4	33700	800
PB-20	T1 Ah M	66800	600	24.5	0.3	1.9	0.2	60	2	5.2	0.7	85	4	29100	900
PB-21	T1 Bfj1 M	81800	600	39.4	0.5	2.7	0.2	68	2	5.5	0.7	115	4	42300	800
PB-22	T1 Bfj2 M	93200	600	52.0	0.5	3.7	0.3	93	2	3.1	0.7	139	5	48200	700
PB-23	T1 C M	87100	600	50.0	0.4	2.5	0.2	86	2	2.0	0.7	119	5	52700	1100
PB-24	T1 Ah T	59000	600	16.7	0.3	3.4	0.2	52	2	7.0	0.7	77	5	24900	1000
PB-25	T1 Bfj1 T	90600	700	44.0	0.4	3.2	0.2	77	3	3.7	0.7	126	5	50800	1200
PB-26	T1 Bfj2 T	89100	600	47.0	0.6	2.5	0.3	85	2	4.2	0.6	135	5	71300	1000
PB-27	T1 Cg T	74000	600	37.4	0.3	1.7	0.2	67	2	2.4	0.6	106	5	142000	2000
PB-28	T1 Om,Ah D	71600	800	10.0	0.3	23.2	0.4	92	4	2.4	0.8	78	7	23300	1100
PB-29	T1 Bog Iron D	39500	400	90.7	0.7	13.9	0.4	63	3	2.5	0.5	60	5	414000	2000
PB-30	T1 Cg D	80000	600	25.0	0.3	2.2	0.2	77	2	2.1	0.6	124	5	31100	900
PB-2	T2 Ah K	69900	600	30.3	0.4	2.4	0.3	53	2	4.0	0.7	92	4	37000	1300
PB-3	T2 Bfj1 K	87000	600	39.2	0.4	2.5	0.2	77	2	3.3	0.6	119	3	48900	1400
PB-4	T2 Bfj2 K	97300	700	40.9	0.5	2.5	0.2	82	2	2.5	0.7	123	4	49800	1400
PB-5	T2 C K	87900	700	36.2	0.5	2.2	0.2	95	2	1.4	0.5	128	4	45800	1500
PB-6	T2 Ah M	60500	600	20.8	0.4	3.0	0.2	53	2	6.5	0.6	85	3	28800	1300
PB-7	T2 Bfj1 M	86500	700	43.9	0.5	2.2	0.2	91	2	5.1	0.4	115	3	47700	1300
PB-8	T2 Bfj2 M	90400	700	51.1	0.6	2.5	0.3	108	3	7.2	0.5	137	4	56800	1500
PB-1	T2 C M	89600	700	49.3	0.5	1.7	0.3	90	2	5.5	1.0	134	5	56300	1600
PB-9	T2 Ah T	63700	600	21.1	0.5	5.6	0.3	82	3	5.4	0.5	83	4	37000	1300
PB-10	T2 Bg1 T	74400	600	28.8	0.5	1.6	0.2	73	2	3.3	0.4	93	3	38000	1200
PB-11	T2 Bg2 T	82800	600	35.5	0.4	1.5	0.2	75	2	3.8	0.5	115	4	41400	1300
PB-12	T2 Cg T	89600	600	46.5	0.5	1.0	0.2	77	2	4.4	0.4	129	4	56900	1400
PB-13	T2 Om,Oh,Ah D	78900	700	12.4	0.5	13.7	0.5	86	3	3.6	0.6	109	5	38700	1500
PB-14	T2 Bog Iron D	74200	700	26.3	0.6	13.9	0.4	71	3	3.0	0.5	104	5	137000	2000
PB-15	T2 Cg D	65800	600	20.0	0.4	2.9	0.3	83	2	1.5	0.4	98	4	96500	1800
PB-31	T3 Ah K	58800	500	16.9	0.4	2.8	0.3	79	2	9.5	0.6	121	4	31700	700
PB-32	T3 Bfj1 K	79000	600	29.7	0.5	2.4	0.2	41	1	8.1	0.5	66	3	44500	700
PB-33	T3 Bfj2 K	82500	600	31.0	0.3	2.4	0.2	82	2	10.7	0.7	105	5	46900	1000
PB-34	T3 C K	82700	600	33.6	0.3	2.3	0.2	92	2	9.4	0.7	113	4	40800	900
PB-35	T3 Ah M	64600	600	18.9	0.4	1.5	0.2	41	2	3.4	0.4	65	3	32300	700
PB-36	T3 Bfj1 M	73400	500	32.1	0.3	2.5	0.2	63	2	6.7	0.6	104	4	41000	900
PB-37	T3 Bfj2 M	85400	600	48.6	0.5	3.1	0.3	88	2	7.6	0.7	134	5	53100	700
PB-38	T3 C M	84300	600	44.6	0.5	2.7	0.3	83	2	5.3	0.6	130	5	50800	700
PB-39	T3 Ah T	72100	600	25.5	0.3	4.4	0.2	80	2	5.5	0.8	93	5	39500	1000
PB-40	T3 Bfjg1 T	84500	600	45.0	0.5	1.4	0.3	76	2	6.7	0.6	121	4	55500	700
PB-41	T3 Bfjg2 T	80700	600	42.9	0.5	1.7	0.3	75	2	6.0	0.7	130	4	66300	800
PB-42	T3 Cg T	86500	600	47.6	0.5	1.2	0.3	76	2	5.8	0.7	128	5	69500	800
PB-43	T3 Om,Ah D	51500	700	10.1	0.5	19.4	0.6	66	3	4.8	0.8	68	6	71900	1200
PB-44	T3 Bog Iron D	42800	500	30.7	0.6	10.3	0.5	40	2	3.0	0.5	87	6	329000	2000
PB-45	T3 Cg D	69800	500	36.1	0.4	3.2	0.3	65	2	3.5	0.5	102	4	77000	1000

Table A-4. Total elements by NAA.

Lab Sample ID	Field Sample ID	Hf	Uncertainty	K	Uncertainty	La	Uncertainty	Mn	Uncertainty	Na	Uncertainty	Rb	Uncertainty	Sb	Uncertainty	Sc	Uncertainty
		($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)
PB-16	T1 Ah K	6.3	0.3	19500	1470	36.2	0.4	120	2	2670	140	176	16	2.1	0.1	10.4	0.1
PB-17	T1 Bfj1 K	5.0	0.3	20000	500	38.4	0.3	58.4	3.1	2260	120	153	15	2.5	0.1	10.8	0.1
PB-18	T1 Bfj2 K	5.3	0.3	25500	590	47.5	0.4	38.6	3.1	1700	120	198	15	3.0	0.1	14.2	0.1
PB-19	T1 C K	3.9	0.3	26900	820	48.8	0.4	29.1	2.8	2100	110	207	12	2.9	0.1	14.8	0.1
PB-20	T1 Ahj M	4.5	0.3	19000	920	32.9	0.4	132	4	2380	120	184	13	1.7	0.1	9.4	0.1
PB-21	T1 Bfj1 M	4.2	0.2	23000	1130	38.7	0.4	54.8	4.1	2090	120	197	12	2.7	0.1	11.4	0.1
PB-22	T1 Bfj2 M	4.7	0.3	30700	1330	50.9	0.5	39.8	1.2	1860	120	243	15	3.6	0.1	15.4	0.1
PB-23	T1 C M	4.0	0.3	28500	670	48.1	0.4	27.9	0.9	2420	130	186	16	4.0	0.1	15.4	0.1
PB-24	T1 Ah T	3.4	0.3	17000	700	28.6	0.4	252	6	2330	160	227	18	1.6	0.1	8.5	0.1
PB-25	T1 Bfj1 T	4.1	0.3	25100	660	42.3	0.4	41.2	3.8	1830	130	213	17	3.6	0.1	13.8	0.1
PB-26	T1 Bfj2 T	3.8	0.3	25100	1180	46.1	0.4	31.5	0.9	1730	110	224	13	3.6	0.1	18.3	0.1
PB-27	T1 Cg T	3.1	0.3	21400	640	37.2	0.3	27.0	0.7	1610	120	167	15	3.3	0.1	13.0	0.1
PB-28	T1 Om,Ah D	2.9	0.4	17100	740	32.8	0.5	26.7	1.8	1720	150	132	20	1.2	0.1	32.6	0.2
PB-29	T1 Bog Iron D	1.7	0.3	6000	780	19.5	0.4	19.1	1.0	637	78	72	19	7.3	0.1	29.7	0.2
PB-30	T1 Cg D	4.0	0.3	21600	690	39.6	0.4	27.3	1.3	2230	130	170	15	2.1	0.1	18.8	0.1
PB-2	T2 Ah K	4.1	0.3	18500	1070	32.5	0.4	106	2	1930	30	174	13	2.1	0.1	9.5	0.1
PB-3	T2 Bfj1 K	4.9	0.2	23000	1000	41.7	0.4	46.0	1.5	1860	30	179	11	3.0	0.1	11.9	0.1
PB-4	T2 Bfj2 K	5.6	0.3	23700	1130	48.0	0.4	28.4	1.3	1650	30	187	11	3.5	0.1	14.7	0.1
PB-5	T2 C K	5.5	0.3	25100	1240	50.5	0.5	25.1	1.3	3280	44	204	13	3.0	0.1	16.3	0.1
PB-6	T2 Ah M	3.6	0.2	18300	1130	28.5	0.4	259	4	2380	40	154	11	1.7	0.1	8.5	0.1
PB-7	T2 Bfj1 M	4.4	0.3	21900	1840	41.5	0.4	60.7	1.9	2400	30	214	12	2.8	0.1	12.1	0.1
PB-8	T2 Bfj2 M	4.9	0.3	29500	2090	48.9	0.5	64.5	1.9	2420	40	222	14	3.9	0.1	15.2	0.1
PB-1	T2 C M	4.6	0.3	29000	1340	49.0	0.5	50.7	1.7	3650	50	223	16	3.4	0.1	16.3	0.1
PB-9	T2 Ah T	4.4	0.3	14100	2100	32.1	0.5	98.5	2.6	2400	40	173	14	1.3	0.1	12.8	0.1
PB-10	T2 Bg1 T	4.1	0.3	18800	1910	33.8	0.4	50.5	1.6	2470	40	197	11	2.1	0.1	11.2	0.1
PB-11	T2 Bg2 T	4.4	0.2	13100	1150	39.6	0.4	50.6	1.7	2480	40	196	12	2.7	0.1	13.7	0.1
PB-12	T2 Cg T	4.9	0.3	25900	1180	42.8	0.4	44.6	1.5	1820	30	187	12	3.7	0.1	14.6	0.1
PB-13	T2 Om,Oh,Ah D	3.8	0.3	19400	1380	36.9	0.5	25.1	1.4	1940	40	146	12	1.3	0.1	39.3	0.2
PB-14	T2 Bog Iron D	3.4	0.4	12600	1430	29.1	0.5	24.2	1.4	1560	30	124	15	2.4	0.1	45.5	0.2
PB-15	T2 Cg D	4.6	0.3	25400	1510	35.0	0.4	22.2	1.2	2270	40	189	13	1.8	0.1	13.7	0.1
PB-31	T3 Ah K	5.1	0.3	20800	1380	43.5	0.4	94.5	1.3	3520	130	202	14	2.7	0.1	13.6	0.1
PB-32	T3 Bfj1 K	2.5	0.2	11800	960	23.1	0.3	126	2	3320	120	127	10	1.3	0.1	6.9	0.1
PB-33	T3 Bfj2 K	4.9	0.3	18800	680	43.0	0.4	126	2	2680	120	157	15	2.9	0.1	15.2	0.1
PB-34	T3 C K	4.3	0.3	22600	730	45.9	0.4	72.0	0.9	3280	120	151	15	2.8	0.1	13.5	0.1
PB-35	T3 Ah M	3.5	0.2	11300	1780	23.7	0.4	391	4	2710	120	123	10	1.6	0.1	6.6	0.1
PB-36	T3 Bfj1 M	3.7	0.2	20100	720	35.1	0.3	77.7	1.7	2790	120	211	14	2.4	0.1	10.7	0.1
PB-37	T3 Bfj2 M	4.6	0.3	26100	1360	47.2	0.4	65.3	3.9	2490	120	197	15	3.4	0.1	14.7	0.1
PB-38	T3 C M	4.4	0.3	29900	1560	46.4	0.4	43.5	6.2	3980	140	185	14	3.2	0.1	16.1	0.1
PB-39	T3 Ah T	4.1	0.3	18400	800	35.7	0.4	65.4	0.9	2280	120	193	15	2.2	0.1	12.1	0.1
PB-40	T3 Bfjg1 T	3.7	0.2	24700	1390	42.9	0.4	57.4	0.9	2380	110	215	12	3.3	0.1	14.2	0.1
PB-41	T3 Bfjg2 T	4.0	0.2	21900	1450	39.9	0.4	58.3	1.5	2080	110	174	13	2.9	0.1	15.7	0.1
PB-42	T3 Cg T	3.4	0.3	24400	1400	41.9	0.4	54.9	1.7	2270	130	182	14	3.5	0.1	14.7	0.1
PB-43	T3 Om,Ah D	2.2	0.4	15200	1620	25.2	0.6	39.3	2.0	1720	150	124	21	1.2	0.1	24.2	0.2
PB-44	T3 Bog Iron D	2.2	0.4	9100	1170	18.7	0.5	20.1	1.1	1020	100	65	20	3.4	0.1	29.9	0.2
PB-45	T3 Cg D	3.7	0.2	22600	1270	34.9	0.4	40.1	1.3	2230	100	171	13	2.5	0.1	12.5	0.1

Table A-4. Total elements by NAA.

Lab Sample ID	Field Sample ID	Sm	Uncertainty	Th	Uncertainty	Ti	Uncertainty	U	Uncertainty	V	Uncertainty	Zn	Uncertainty
		($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)
PB-16	T1 Ah K	3.78	0.05	9.8	0.3	4320	250	3.9	0.3	177	5	196	22
PB-17	T1 Bfj1 K	3.61	0.03	10.0	0.3	4410	220	3.6	0.2	246	5	143	21
PB-18	T1 Bfj2 K	4.35	0.03	14.2	0.3	5010	250	5.0	0.2	303	5	84	20
PB-19	T1 C K	4.77	0.04	13.3	0.3	4760	220	4.6	0.2	314	5	80	16
PB-20	T1 Ahj M	3.12	0.03	7.9	0.3	4860	250	3.0	0.2	200	4	156	17
PB-21	T1 Bfj1 M	3.41	0.04	9.9	0.2	4670	250	3.9	0.2	259	5	152	16
PB-22	T1 Bfj2 M	4.94	0.04	16.5	0.3	4870	230	5.6	0.2	333	5	99	18
PB-23	T1 C M	5.23	0.04	14.4	0.3	4530	240	4.7	0.2	303	5	78	20
PB-24	T1 Ah T	3.05	0.03	6.8	0.3	4710	300	3.1	0.2	181	5	74	23
PB-25	T1 Bfj1 T	5.15	0.04	11.6	0.3	4640	260	4.5	0.2	317	6	93	22
PB-26	T1 Bfj2 T	5.59	0.04	14.4	0.3	4550	230	5.5	0.2	313	5	141	17
PB-27	T1 Cg T	4.24	0.03	10.0	0.3	4100	240	3.8	0.2	249	5	81	18
PB-28	T1 Om,Ah D	24.5	0.1	13.1	0.5	2800	270	14.6	0.3	175	5	130	28
PB-29	T1 Bog Iron D	14.0	0.1	11.8	0.4	1240	150	7.8	0.3	142	4	150	21
PB-30	T1 Cg D	7.24	0.04	12.1	0.3	4290	240	7.0	0.2	243	5	98	19
PB-2	T2 Ah K	3.13	0.04	9.9	0.3	4310	230	3.4	0.2	215	5	130	17
PB-3	T2 Bfj1 K	3.65	0.04	12.5	0.3	4410	220	4.5	0.2	274	5	59	12
PB-4	T2 Bfj2 K	4.36	0.04	15.8	0.3	5400	240	6.3	0.2	301	5	50	12
PB-5	T2 C K	5.67	0.04	14.2	0.3	5070	240	6.2	0.2	283	6	44	14
PB-6	T2 Ah M	2.94	0.03	7.2	0.3	3480	240	2.8	0.2	184	5	95	14
PB-7	T2 Bfj1 M	3.63	0.04	11.5	0.2	4910	240	4.4	0.2	288	5	125	12
PB-8	T2 Bfj2 M	4.49	0.05	14.9	0.3	4710	250	5.9	0.2	317	6	118	13
PB-1	T2 C M	4.74	0.05	16.7	0.4	4740	240	6.7	0.3	312	6	129	21
PB-9	T2 Ah T	13.2	0.1	7.8	0.3	3860	240	4.7	0.2	190	5	84	14
PB-10	T2 Bg1 T	5.47	0.04	8.0	0.2	4660	220	3.7	0.2	239	5	93	11
PB-11	T2 Bg2 T	4.75	0.04	10.9	0.3	4860	230	3.9	0.2	259	5	114	13
PB-12	T2 Cg T	4.90	0.03	13.3	0.3	4850	220	3.8	0.2	327	5	101	12
PB-13	T2 Om,Oh,Ah D	13.3	0.1	13.6	0.4	3520	260	19.3	0.3	205	5	150	16
PB-14	T2 Bog Iron D	10.8	0.1	13.3	0.3	3490	250	15.5	0.3	192	5	203	17
PB-15	T2 Cg D	5.49	0.04	10.4	0.3	3920	220	4.4	0.2	202	5	95	13
PB-31	T3 Ah K	4.21	0.04	12.7	0.3	3910	220	3.5	0.2	166	4	218	19
PB-32	T3 Bfj1 K	2.32	0.03	6.7	0.2	3440	210	2.2	0.2	213	4	150	13
PB-33	T3 Bfj2 K	6.00	0.04	14.7	0.3	3930	220	6.2	0.2	220	4	174	20
PB-34	T3 C K	8.06	0.04	13.3	0.3	4470	210	5.2	0.2	263	5	106	20
PB-35	T3 Ah M	2.34	0.03	5.8	0.2	3750	230	2.3	0.2	191	4	107	12
PB-36	T3 Bfj1 M	3.28	0.03	10.5	0.3	4220	220	3.4	0.2	227	4	168	18
PB-37	T3 Bfj2 M	4.59	0.04	14.5	0.3	4170	230	5.7	0.2	303	5	155	18
PB-38	T3 C M	4.96	0.04	14.2	0.3	4710	230	6.0	0.2	302	5	135	18
PB-39	T3 Ah T	12.3	0.1	10.1	0.3	4310	230	5.2	0.2	223	5	139	19
PB-40	T3 Bfjg1 T	5.73	0.04	12.0	0.3	4520	210	4.2	0.2	307	5	169	15
PB-41	T3 Bfjg2 T	4.85	0.05	13.2	0.3	4340	220	4.4	0.2	279	5	168	16
PB-42	T3 Cg T	4.67	0.04	13.6	0.3	4820	240	4.0	0.2	304	5	146	17
PB-43	T3 Om,Ah D	13.7	0.1	11.3	0.5	2530	280	21.0	0.4	137	5	140	26
PB-44	T3 Bog Iron D	11.5	0.1	11.3	0.4	2410	210	14.0	0.3	147	4	137	22
PB-45	T3 Cg D	5.39	0.04	10.3	0.3	4150	210	3.6	0.2	235	4	93	15

Notes: value for As is from 559 keV peak
value for Fe is from 1100 keV peak
value for La is from 487 keV peak
value for Sc is from 889 keV peak
value for U is from 278 keV peak
value for Br is from 554 keV peak

Table A-5. Standards data by NAA.

Lab Sample ID	ALUMINUM				ARSENIC				BROMINE		CERIUM		COBALT		CHROMIUM		IRON	
	Al	Uncertainty	Concensus Value	Uncertainty	As	Uncertainty	Concensus Value	Uncertainty	Br	Uncertainty	Ce	Uncertainty	Co	Uncertainty	Cr	Uncertainty	Fe	Uncertainty
	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)
NIST 1645[1]	25900	300	22600	400	71.2	0.6	66	5	2.5	0.2	179	4	6.4	0.5	27995	30	10200	2000
NIST 1633a[2]	143000	800	143000	800	146	1	146	4	—	—	—	—	—	—	—	—	—	—
SCo-1[3]	74200	600	72300	1100	13.1	0.4	—	—	0.6	0.2	71	2	9.4	0.5	70	3	36500	1300
SCo-1*	—	—	—	—	11.4	0.4	—	—	1.56*	0.4	65	2	8.6	0.5	67	3	37300	1300
NIST 1646[4]	—	—	—	—	10.2	0.4	—	—	117	1.0	81	3	10.4	1.0	78	6	34200	900
NIST 1646*	—	—	—	—	10.7	0.5	11	1	118	1.0	73	3	8.5	1.3	72	6	33100	800
SO-2[5]	—	—	—	—	1.17	0.36	1.17	0.26	—	—	—	—	—	—	—	—	—	—

Table A-5. Standards data by NAA.

Lab Sample ID	HAFNIUM		POTASSIUM		LANTHANUM		MANGANESE				SODIUM				RUBIDIUM		ANTIMONY	
	Hf	Uncertainty	K	Uncertainty	La	Uncertainty	Mn	Uncertainty	Concensus Value	Uncertainty	Na	Uncertainty	Concensus Value	Uncertainty	Rb	Uncertainty	Sb	Uncertainty
	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)
NIST 1645[1]	1.2	0.2	11500	1300	8.6	0.3	724	6	752	46	5410	60	5300	500	59	10	79.1	0.3
NIST 1633a[2]	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SCo-1[3]	4.7	0.3	24700	1860	31.4	0.4	394	5	408	30	6580	30	6670	460	162	15	4.7	0.1
SCo-1*	4.0	0.3	23100	2660	31.1	0.4	—	—	—	—	—	—	—	—	149	14	4.5	0.1
NIST 1646[4]	10.2	0.4	21400	1980	37.4	0.5	—	—	—	—	—	—	—	—	101	30	0.5	0.1
NIST 1646*	9.5	0.4	20100	3080	38.0	0.5	—	—	—	—	—	—	—	—	114	25	0.9	0.1
SO-2[5]	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Table A-5. Standards data by NAA.

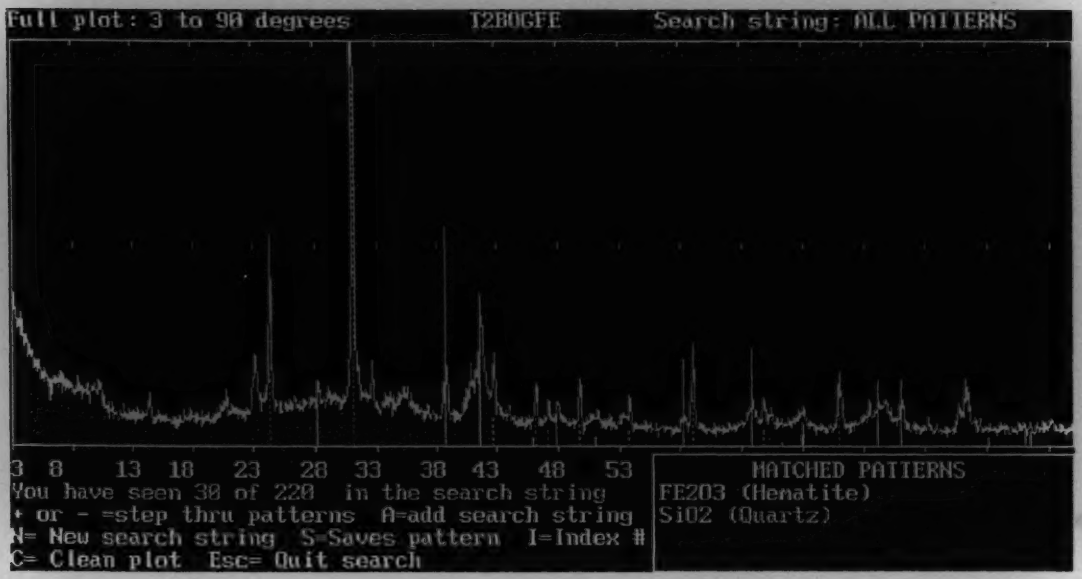
Lab Sample ID	SCANIUM		SAMARIUM		THORIUM		TITANIUM				URANIUM		VANADIUM				ZINC	
	Sc	Uncertainty	Sm	Uncertainty	Th	Uncertainty	Ti	Uncertainty	Concensus Value	Uncertainty	U	Uncertainty	V	Uncertainty	Concensus Value	Uncertainty	Zn	Uncertainty
	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)
NIST 1645[1]	1.9	0.05	1.45	0.05	6.6	0.3	2080	200	600	100	1.2	0.3	23.1	1.9	25	4	1383	26
NIST 1633a[2]	—	—	—	—	—	—	8490	320	8130	480	—	—	296	6	296	14	—	—
SCo-1[3]	11.3	0.1	5.15	0.04	9.3	0.2	3550	250	3760	390	3.3	0.2	138	4	131	13	82	16
SCo-1*	11.3	0.1	5.08	0.05	9.4	0.2	—	—	—	—	3.1	0.2	—	—	—	—	128	15
NIST 1646[4]	10.5	0.1	6.55	0.05	11.0	0.4	—	—	—	—	3.3	0.3	—	—	—	—	167	38
NIST 1646*	10.4	0.1	6.71	0.06	10.6	0.4	—	—	—	—	3.2	0.3	—	—	—	—	137	31
SO-2[5]	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Notes: [1]National Institute of Standards and Technology river sediment
[2]National Institute of Standards and Technology flyash
[3]United States Geological Survey Cody Shale
[4]National Institute of Standards and Technology estuarine sediment
[5]CANMET Podzolic B horizon soil
*Second measurement of same sample following an additional decay of one day.
value for As is from 559 keV peak
value for Fe is from 1100 keV peak
value for La is from 487 keV peak
value for Sc is from 889 keV peak
value for U is from 278 keV peak
value for Br is from 554 keV peak, except * = entered 776 peak value

Table A-6. Comparison of various elements in Alberta soils.

Element	Units	Crustal Abundance (shale) [1]	Average Elemental Concentration in C Horizon Acid Sulfate Soil (current study) [2]	Average Elemental Concentration in Boundary Soil Parent Material (Bulmer, 1987) [3]	Average Concentration in Central Albertan Calcareous Till Parent Material (Warren, 1991) [4]	Representative Elemental Concentration in Ck2 Horizon (36% clay) of Central Albertan Gray Luvisol (Dudas and Pawluk, 1980) [5]
Al	($\mu g\ g^{-1}$)	80000	82400	80000	—	—
Fe	($\mu g\ g^{-1}$)	47000	61200	48000	—	—
K	($\mu g\ g^{-1}$)	23000	25300	—	—	—
Na	($\mu g\ g^{-1}$)	6600	2600	4000	—	—
Ti	($\mu g\ g^{-1}$)	4500	4530	4075	—	—
V	($\mu g\ g^{-1}$)	130	278	240	86	—
Rb	($\mu g\ g^{-1}$)	140	185	160	54	—
Cr	($\mu g\ g^{-1}$)	100	120	110	37	—
Zn	($\mu g\ g^{-1}$)	80	98.9	107	46.0	62.0
Ce	($\mu g\ g^{-1}$)	50	81.8	71	38.1	—
La	($\mu g\ g^{-1}$)	40	43.3	41.2	23.5	—
Mn	($\mu g\ g^{-1}$)	850	38.7	23.8	360	—
As	($\mu g\ g^{-1}$)	6.6	38.5	36.5	4.9	5.8
Sc	($\mu g\ g^{-1}$)	10	15.0	16.5	5.7	—
Th	($\mu g\ g^{-1}$)	11	13.0	11.5	6.1	—
Sm	($\mu g\ g^{-1}$)	6.5	5.45	4.3	2.86	—
U	($\mu g\ g^{-1}$)	3.2	5.0	5.2	2.7	—
Hf	($\mu g\ g^{-1}$)	6	4.2	4	3.5	—
Co	($\mu g\ g^{-1}$)	20	3.8	3.5	6.0	9.9
Sb	($\mu g\ g^{-1}$)	1.5	3.0	1.4	1.0	—
Br	($\mu g\ g^{-1}$)	6	2.15	0.7	—	—

Notes:
[1] from Taylor and McLellan, 1985.
[2] from the current document; values are average of all C horizon samples
[3] from Bulmer, C. 1987. Nutrient imbalances of aspen poplar in acid sulfate soils in northwestern Alberta. Master of Science Thesis, University of Alberta, Edmonton, Alberta.
[4] from Warren, C.J. 1991. Weathering, trace elements, and smectite stability in extremely acid soil environments. Doctor of Philosophy Thesis, University of Alberta, Edmonton, Alberta.
[5] from Dudas, M.J. and S. Pawluk. 1980. Natural abundances and mineralogical partitioning of trace elements in selected Alberta soils. Can. J. Soil Sci. 60: 763-771.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Search string: ALL PATTERNS
3 8 13 18 23 28 33 38 43 48 53
You have seen 30 of 220 in the search string
+ or - =step thru patterns A=add search string
N= New search string S=Saves pattern I=Index #
C= Clean plot Esc= Quit search
MATCHED PATTERNS
FE2O3 (Hematite)
SiO2 (Quartz)

Figure A-1. X-ray diffractogram of Bog Iron soil from Transect 2.

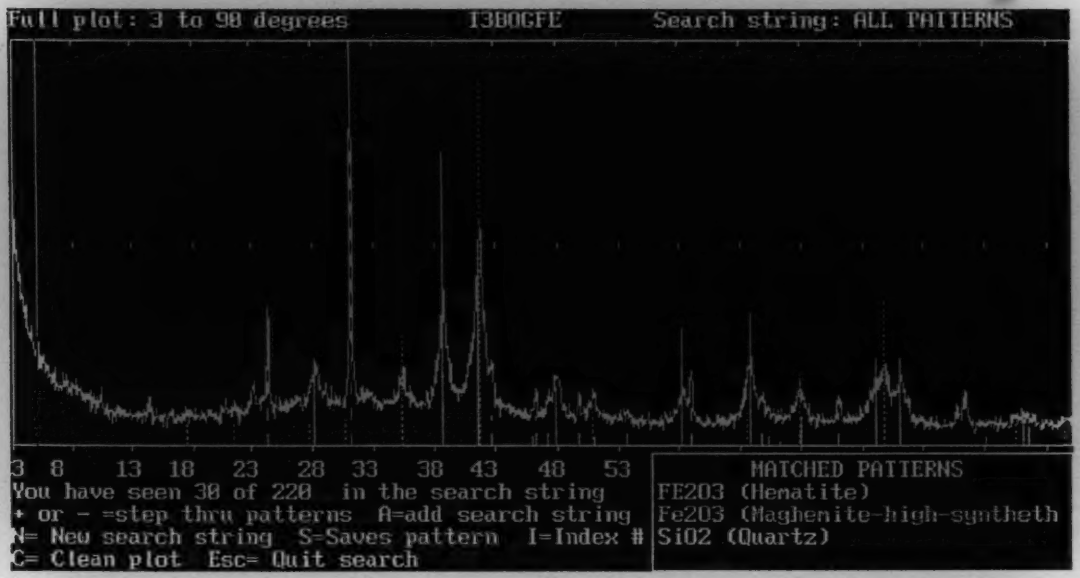
Full plot: 3 to 90 degrees
I3BOGFE
Search string: ALL PATTERNS
3 8 13 18 23 28 33 38 43 48 53
You have seen 30 of 220 in the search string
+ or - =step thru patterns A=add search string
N= New search string S=Saves pattern I=Index #
C= Clean plot Esc= Quit search
MATCHED PATTERNS
FE2O3 (Hematite)
Fe2O3 (Maghenite-high-syntheth
SiO2 (Quartz)

Figure A-2. X-ray diffractogram of Bog Iron soil from Transect 3.